

Phase change solvents for post-combustion CO₂ capture: Principle, advances, and challenges

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HIGHLIGHTS

- Both liquid–solid and liquid–liquid phase change solvents critically reviewed.
- Various mechanisms triggering phase separations in solvents elucidated in detail.
- Advantages and challenges of phase change processes for CO₂ capture assessed.
- Gaps between state-of-the-art and ideal solvents analyzed.
- Insights into research needs regarding solvents and desired properties provided.

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ABSTRACT

Carbon Capture and Storage is regarded as an important component in a portfolio of low-carbon energy technologies for mitigating climate change. Absorption technologies are presently the most available and effective approach for post-combustion CO₂ capture. However, state-of-the-art amine-based absorption technologies incur intensive energy use, as high as 3 times the thermodynamic minimum, thus resulting in prohibitively high costs. Solvents are key to the performance of absorption technologies. Recently, a new class of solvents, phase change solvents, have attracted growing interest due to their potential to substantially reduce energy use for CO₂ capture. Phase change solvents are homogeneous (single-phase) solvents under normal conditions, but undergo a phase transition into a heterogenic (two-phase) system, triggered by changes in polarity, hydrophilicity, ionic strength, or hydrogen bond strength to form a CO₂-lean liquid phase and a CO₂-enriched liquid or solid phase. This review paper first examines different mechanisms that trigger phase separations in solvents. A comprehensive list of phase change solvents reported in the recent literature, including those subject to chemically or thermally triggered phase changes, non-aqueous or aqueous systems, and those forming either a CO₂-enriched solid or a liquid phase are provided and their physiochemical properties for CO₂ capture are discussed. Enabled by phase change solvents, different variants of CO₂ absorption processes have been developed and tested in laboratory or pilot scales over the past ten years. The status of such emerging processes is summarized and their advantages and challenges for post-combustion CO₂ capture are reviewed and commented. Solvent properties such as CO₂ loading capacity, lean- and rich-phase partition, desorption pressure, absorption kinetics, viscosity, stability, and volatility are critical for both CO₂ capture performance and scalability. Gaps between state-of-the-art and ideal solvents are analyzed, and insights into the research needs such as solvent structure–property–performance relations, computational solvent design, ideal vapor–liquid

Abbreviations: AMP, aminomethyl propanol; BDA, 1,4-butanediamine; CAPEX, capital expenditure; DBA, dibutylamine; DEA, diethanolamine; DEEA, 2-(diethylamino)-ethanol; DETA, diethylenetriamine; DIPA, diisopropylamine; DMCA, N,N-dimethylcyclohexylamine; DPA, dipropylamine; DsBA, disecbutylamine; e-NRTL, electrolyte–nonrandom two liquids; LCST, lower critical phase solution temperature; MAPA, N-methyl-1,3-propane-diamine; MCA, N-methylcyclohexylamine; MEA, monoethanolamine; MMEA, monomethylethanolamine; NMP, N-methyl-2-pyrrolidone; NMR, nuclear magnetic resonance; OPEX, operational expenditure; PCC, post-combustion carbon capture; PMDETA, pentamethyldiethylenetriamine; ProK, potassium proline; RSF, recycle split fraction; RTIL, room-temperature ionic liquids; TAU, potassium taurate; TBS, thermomorphic biphasic solvents; TEGDME, triethylene glycol dimethyl ether; TETA, triethylenetetramine; TRL, technology readiness level; USDOE, U.S. department of energy; VLE, vapor–liquid equilibrium; XRD, X-ray diffraction

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equilibrium behavior, and integration of capture processes with post-combustion emission sources are provided.

1. Introduction

Carbon dioxide (CO₂) is a major greenhouse gas, accounting for 77% of total global emissions. Excessive CO₂ emissions contribute to global warming. Most of the CO₂ is emitted as a by-product of fossil fuel use and cement manufacturing [1–5]. To mitigate global warming, in 2015 approximately 200 countries agreed to adopt the Paris Agreement, which would cut CO₂ emissions in an effort to cap the global average temperature increase at less than 2 °C. According to the Agreement, China committed to cap CO₂ emissions by 2030 and lower the CO₂ intensity (CO₂ emissions per unit of GDP) by 60% to 65% from the 2005 level [6,7].

CO₂ capture has been regarded as a crucially important measure to control the emissions of CO₂ produced by fossil fuel combustion. In general, CO₂ can be captured by three major process options: post-combustion, pre-combustion and oxy-fuel combustion capture [2,8–11]. Among them, post-combustion carbon capture (PCC) is considered the most effective method for reducing CO₂ emissions in the near term because the requirements for retrofitting existing facilities are minimal [12,13]. The challenge of PCC from a separation perspective is that the flue gas from conventional fossil fuel combustion has a relatively low CO₂ concentration (e.g., 10–15 vol% from coal-fired boilers and 4–7 vol% from natural gas-fired boilers) and a low pressure (i.e., near atmospheric pressure). This results in a low driving force for CO₂ separation (i.e., low CO₂ partial pressure) and a large volume of gas to be treated [14]. Consequently, PCC requires intensive energy use and tends to incur a large equipment footprint and high cost.

Chemical absorption is widely used for carbon capture in industry compared with other technologies such as adsorption and membranes [15]. Among various absorption technologies [16–18], the monoethanolamine (MEA)-based absorption process is presently the industrial benchmark for PCC [19,20]. According to a U.S. Department of Energy (USDOE) study [21], CO₂ capture at a pulverized coal-fired power plant equipped with the MEA process will increase the cost of electricity by 85% for a subcritical power plant and 81% for a supercritical plant. A majority of the cost of electricity increase is attributable to parasitic power loss (55.4%), followed by capital costs (25.3%) and then by operation and maintenance costs (19.3%) [22]. Note that the costs associated with parasitic power loss account for the capital cost due to an increase in power plant size and the operation & maintenance cost due to extra fuel usage because of carbon capture. Clearly, the intensive energy use and high cost of the MEA process present huge challenges for large-scale deployment of PCC.

The minimum work required for CO₂ separation and compression at coal-fired power plants has been estimated at 0.116 kWh/kg of CO₂ captured [14]. Given the typical CO₂ emission intensity of 0.9 kg/kWh, this translates to a 10.4% reduction in net power output. In comparison, the parasitic power loss for the benchmark MEA process has been estimated at approximately 0.32 kWh/kg of CO₂ captured, resulting in a 29% reduction in net output [14]. Obviously, sizable potential exists for improving the energy efficiency of PCC.

Research and development efforts have grown substantially for PCC in recent years. In an Electric Power Research Institute study, 125 PCC technologies were reviewed and a Technology Readiness Level (TRL) score was assigned to describe different stages of development, from conceptual analysis (TRL1) to commercial deployment (TRL9) [23,24]. Among these technologies, 43% were based on absorption processes, 23% on adsorption and 14% on membranes. Most of the projects reviewed were laboratory-, bench- or small pilot-scale developments, and only four absorption projects were at the sub- or full-scale

demonstration stage. Amine-based absorption processes for removing CO₂ from gas streams have been applied in the chemical and oil industries for more than 80 years [25,26], and scale-up of these processes for the PCC application is expected to present few technical obstacles. However, state-of-the-art amine-based processes are still energy intensive and costly because of their intensive heat use for solvent regeneration and solvent degradation over time. Present research and development efforts for absorption are focused on addressing these issues through the development of novel solvents, new stripping process configurations, high-pressure processes and hybrid systems [14,18,27–33].

Recently, phase transitional solvents have attracted increased interest for their potential to substantially reduce both energy use and equipment costs for CO₂ capture [34–38]. Wang and Li provided an earlier overview of phase change solvents for CO₂ capture [39]. Another review of biphasic solvent research over a period of ten years (until 2016) was provided by Zhuang et al. with a focus on technical information of four technologies [40]. Biphasic solvents are homogeneous (single-phase) solvents before CO₂ is loaded or the temperature is changed. Upon CO₂ absorption or a temperature shift, they form a heterogenic (two-phase) system, with a CO₂-enriched phase and a CO₂-lean phase. The CO₂-lean phase is a liquid phase and the CO₂-enriched phase can be either a liquid or solid phase.

Because only the CO₂-enriched liquid phase is used for solvent regeneration, the mass of solvent that requires regeneration is decreased [41–43]. Consequently, the heat required to heat the solvent (*sensible heat*) is reduced. According to the phase equilibrium principle, a high CO₂ loading in the CO₂-enriched solvent phase generates a higher partial pressure of CO₂, which translates to a higher CO₂-to-water vapor pressure ratio in the stripping product gas stream, thus reducing the heat use associated with water vaporization (*stripping heat*). Moreover, a high partial pressure of CO₂ results in a high total stripping pressure, reducing the mechanical compression requirement for CO₂ compression (*compression work*). Furthermore, the biphasic solvent may be tuned with a lower heat of desorption (*reaction heat*) than that of MEA (~80 kJ/mol) while still maintaining the required solvent performance. Therefore, biphasic solvents may reduce all the heat use elements (i.e., sensible heat, stripping heat and reaction heat) for solvent regeneration and the work requirement for CO₂ compression. It has been reported that the energy penalty associated with biphasic solvent-enabled processes can be reduced to 0.22–0.25 kWh/kg of CO₂ [44–47]. In addition, because of the lower mass of solvent for CO₂ stripping and the reduced need for downstream mechanical compression of CO₂, the related equipment costs may be reduced.

This review presents the principles of liquid–solid and liquid–liquid phase transitions in CO₂ absorption systems and summarizes comprehensive advances in the development of phase change solvents and the processes they enable. The review further assesses issues associated with solvent property limitations, solvent management and process equipment to provide insights into future research and development needs.

2. Mechanism of biphasic solvents for CO₂ absorption

2.1. CO₂-triggered biphasic solvents

CO₂-triggered biphasic solvents were initially developed for green chemistry processes. In many industrial processes, it is preferable to perform consecutive chemical reactions or physical processes, with

different solvent properties required at different stages [48,49]. A CO₂-triggered switchable solvent is a liquid that is reversible between two states with distinct properties, such as ionic strength, hydrophilicity or viscosity [49,50]. This type of solvent uses a nitrogenous base, such as an amine, amidine or guanidine, as an “additive”. The “switching on” step of the solvent proceeds as CO₂ reacts with the additive, leading to protonation of the additive, the formation of a salt and a change in solvent properties [49,51]. To recover the original liquid (“switching off”), the CO₂ is stripped from the liquid by heating or purging an inert gas, or both. Depending on the property to be switched, CO₂-triggered solvents are categorized into switchable polarity, switchable water and switchable hydrophilicity solvents. Switchable hydrophilicity solvents are limited to only a few aqueous solutions of amine-like compounds (e.g., N-ethylpiperidine or triethylamine) and thus are not common

[52]. In comparison, both switchable polarity and switchable water solvents have been researched for CO₂ capture applications.

2.1.1. Switchable polarity

Switchable polarity solvents, which are usually nonaqueous, can change reversibly from a low-polarity to a high-polarity form triggered by the dissolution of CO₂. Amidine/alcohol mixtures, guanidine/alcohol mixtures, amidine/amine mixtures, secondary amines, diamines and guanidine/acidic alcohol mixtures are typical switchable polarity solvents (Fig. 1) [48,49,53]. Because of the solubility difference of solutes in different solvents, a polarity switch can result in liquid–liquid phase separation or the precipitation of products.

In general, switchable polarity solvents that form carbamates (from amine and CO₂ reactions) and alkylcarbonates (from amidine/

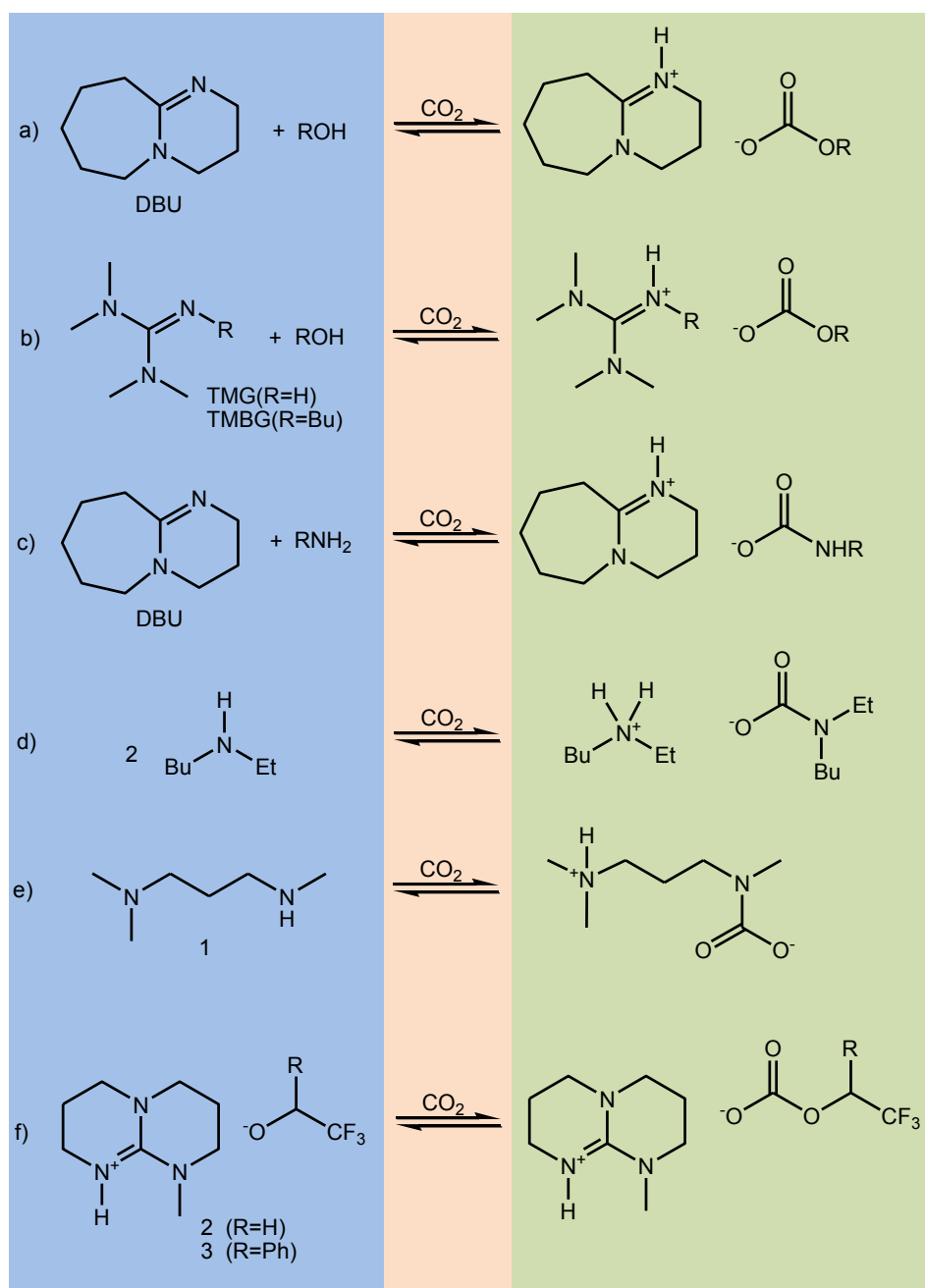
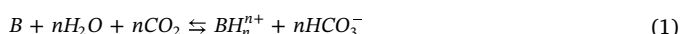


Fig. 1. Typical switchable-polarity solvents: (a) amidine/alcohol mixtures, (b) guanidine/ alcohol mixtures, (c) amidine/amine mixtures, (d) secondary amines, (e) a diamine, and (f) guanidine/acidic alcohol mixtures. The blue color illustrates the low-polarity form of the solvent, whereas the green color illustrates the high-polarity form of the solvent [48]. Adapted from Ref. [43] with permission from Springer Nature.

guanidine and CO₂ reactions) can be used for CO₂ separation from low-pressure gas streams such as flue gas [49,54]. However, amidines and guanidines are expensive; thus, their practicability for CO₂ capture is still questionable. In comparison, amines are both nucleophiles and proton donors and can serve as single-component switchable polarity solvents, potentially resulting in a low cost for CO₂ capture.

2.1.2. Switchable water

A switchable water solvent is an aqueous solution with switchable ionic strength, typically containing an ionogen, a compound that does not exist as ions but becomes ionic when the CO₂ is dissolved in water [53]. Initially, a fresh aqueous solution with a nitrogenous base is low in ionic strength acquired through the dissociation of water. After reacting with CO₂, the base is converted to a bicarbonate salt, resulting in a dramatic increase in ionic strength, as shown in Eqs. (1) and (2) [55].



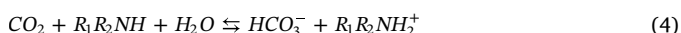
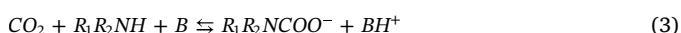
$$I = \frac{1}{2}m(n^2 + n) \quad (2)$$

where B is the nitrogenous base, n is the number of protonatable sites on base B , m is the molality of the base in the solution and I is the ionic strength. Water switching can lead to liquid–liquid phase separation in a homogeneous mixture of water and organic solvent via the salting-out effect [56] or cosolvent effect [57].

According to Eq. (2), with an increasing number of protonatable sites (n) on the base, the ionic strength can be substantially increased, resulting in an organic compound with a high separation tendency [55,58,59]. It has been reported that triamines are more effective than diamines, which themselves are more effective than monoamines, for the salting-out effect. However, a further increase in protonatable sites does not necessarily increase the effectiveness for phase separation because it may also change other contributing factors, such as the molecular weight and hydrophobicity of the base [58].

2.2. Thermomorphic biphasic solvents

Thermomorphic biphasic solvents (TBS) are typically mixtures of lipophilic amines and water. A fresh TBS can be a biphasic or homogeneous system, depending on the miscibility between water and the lipophilic amines. After a certain amount of CO₂ is loaded to the TBS, it encounters a phase separation or remains homogeneous. The overall reactions between a primary or secondary amine and CO₂ can be expressed as follows [60]:



where R is an organic group or hydrogen atom and B is a base (e.g., a CO₂-free amine). The overall reaction between a tertiary amine and CO₂ can be expressed as [61]



The carbamate formed from the reaction of the primary or secondary amine with CO₂ has moderate solubility in either water or the lipophilic amine. The bicarbonate has good polarity such that it can easily be dissolved in water. The solubility of a CO₂-free amine in water relies on hydrogen bonds between the amine and water molecules. The TBS system generally has four types of hydrogen bonds, listed in order of bond energy strength from strong to weak: OH–O, OH–N, NH–N and NH–O [62]. Increasing the temperature can break the intermolecular hydrogen bonds between two molecules, beginning from bonds with a weak to strong energy strength.

Fig. 2 illustrates the phase transition of an aqueous neat amine solution resulting from an elevation in temperature. T_1 denotes the initial temperature. As the temperature is increased, the hydrogen bond of NH–O breaks at T_2 and that of NH–N breaks at T_3 . As the temperature is

increased further to T_4 , the hydrogen bond of OH–N breaks, and then the self-associated nature of water forces the amine out of the solution, forming dual phases. The temperature, at which the phase separation of a mixture of lipophilic amine and water is triggered, is the lower critical phase solution temperature (LCST) [60]. Fig. 3 illustrates the phase transition after the TBS is loaded with CO₂. In scenario one (S_1), the CO₂ is absorbed into the solution. The reaction of the amine with CO₂ generates a bicarbonate and carbamate, both of which dissolve in the solution, as shown in S_2 , resulting in the formation of a homogeneous phase. After the temperature is increased until the hydrogen bonds break (Fig. 2), the homogeneous phase splits into two liquid phases, as illustrated in S_3 . The upper phase is an organic phase (CO₂-lean amine) and the lower phase is an aqueous solution composed of the bicarbonate and carbamate.

3. Biphasic solvents applied for CO₂ capture

3.1. CO₂-triggered biphasic solvents

CO₂-triggered biphasic solvents can be either nonaqueous or aqueous. Advances made in the development of these two groups of biphasic solvents can be summarized as follows.

3.1.1. Nonaqueous biphasic solvents

The stripping heat attributable to water evaporation during CO₂ desorption has been estimated to account for approximately 27% of the total energy penalty in the benchmark MEA process [63]. Nonaqueous solvents have been used in an attempt to deplete the stripping heat because of the lower vaporization heat of the organic solvent compared with water [64]. Because water is replaced with organic solubilizers or ionic liquids and the stripping temperature required for solvent regeneration is relatively low, nonaqueous solvents are able to overcome several disadvantages associated with aqueous absorbents, such as excess amine degradation and evaporation losses, equipment corrosion and the high heat duty required for solvent regeneration [65]. Typically, the selection of organic solubilizers should meet the following criteria: (1) have a high boiling point, (2) have a low heat capacity, (3) have low viscosity and (4) avoid foaming. The phase separation that occurs in the nonaqueous solvent is due to its switchable polarity. Upon CO₂ absorption, a carbamate is produced, resulting in a significant increase in solvent polarity. Once the carbamate becomes immiscible with the organic solubilizer, phase separation occurs.

3.1.1.1. Amine–alcohol solvents. Various individual alcohols [e.g., ethanol, 1-propanol, 1-heptanol, 1-octanol, isooctanol, decylalcohol, 1,2-propandiol, 2-thoxyethanol and 2-(2-methoxyethoxy)ethanol], their blends (e.g., ethylene glycol-ethanol/methanol/1-propanol, 1,2-propandiol/ethanol/methanol), and several other organic solvents [e.g., N,N-Dimethylformamide (DMF)] have been tested to replace water as solubilizers because of their low cost and commercial availability (see Table 1) [66–76]. Long-chain alcohols, polyethers, and alcohol blends are generally considered to be beneficial for promoting phase separation [77,78]. Among them, alcohol blends have mainly been used to obtain a tradeoff between individual alcohols for the viscosity or boiling point. As shown in Table 1, primary, secondary and sterically hindered amines and their blends with tertiary amines have been tested for CO₂ absorption.

In the nonaqueous amine–alcohol solvents, the CO₂ can react only with the primary or secondary amines via the carbamic acid reaction mechanism [79]:



The carbamic acid formed can be deprotonated by a base, such as the excess amine:



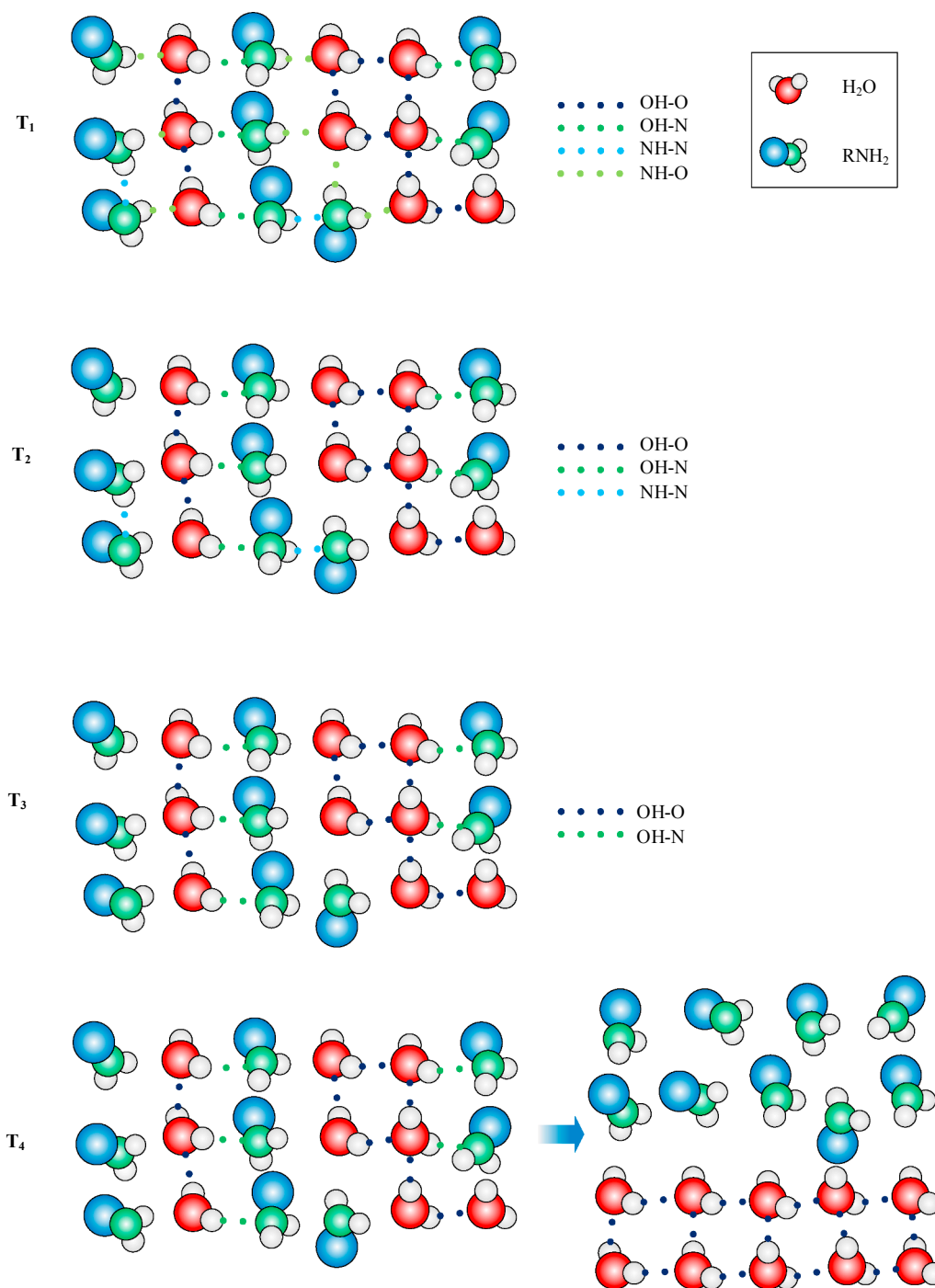
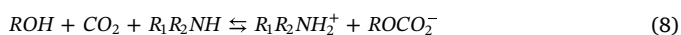


Fig. 2. Phase transition of a neat thermomorphoric amine aqueous solution in the course of a temperature increase from T_1 to T_2 , to T_3 , and to T_4 .

Note that tertiary amines cannot react directly with CO_2 under non-aqueous conditions; however, they can serve as bases for carbamic acid deprotonation, as shown in Eq. (7). Furthermore, in nonaqueous amine–alcohol solvents, an alcohol (ROH) may participate in CO_2 absorption in the presence of a primary or secondary amine to produce an alkyl carbonate ($ROCO_2^-$), which has been confirmed by ^{13}C nuclear magnetic resonance (NMR) analysis [69]:



The formation of alkyl carbonate will enhance the absorption capacities of the tested solvents, given that the stoichiometry (1.0) of the CO_2 –alcohol reaction is twice that of the CO_2 –primary or secondary amine reaction (0.5).

Depending on the properties of alcohols, amines and the formed carbamates, two types of phase separation, liquid–liquid and liquid–solid phase separation, can occur upon loading of CO_2 [67–70]. Hu [80] reported that more than 80% of the captured CO_2 was enriched in the rich phase, which was required for regeneration. Hu [81] also observed that, in general, a long-chain alcohol, such as 1-heptanol, 1-octanol, isooctanol or decylalcohol, as a solubilizer could induce liquid–liquid phase separation. However, the alkyl carbonate was not detected by ^{13}C NMR analysis because the weak acidity of the long-chain alcohol prevented the reaction, as depicted in Eq. (8). For example, a group of proprietary CO_2 self-concentrating amine blends with isooctanol or decylalcohol developed by the 3H Company formed two distinct liquid phases upon absorbing CO_2 [66], although detailed

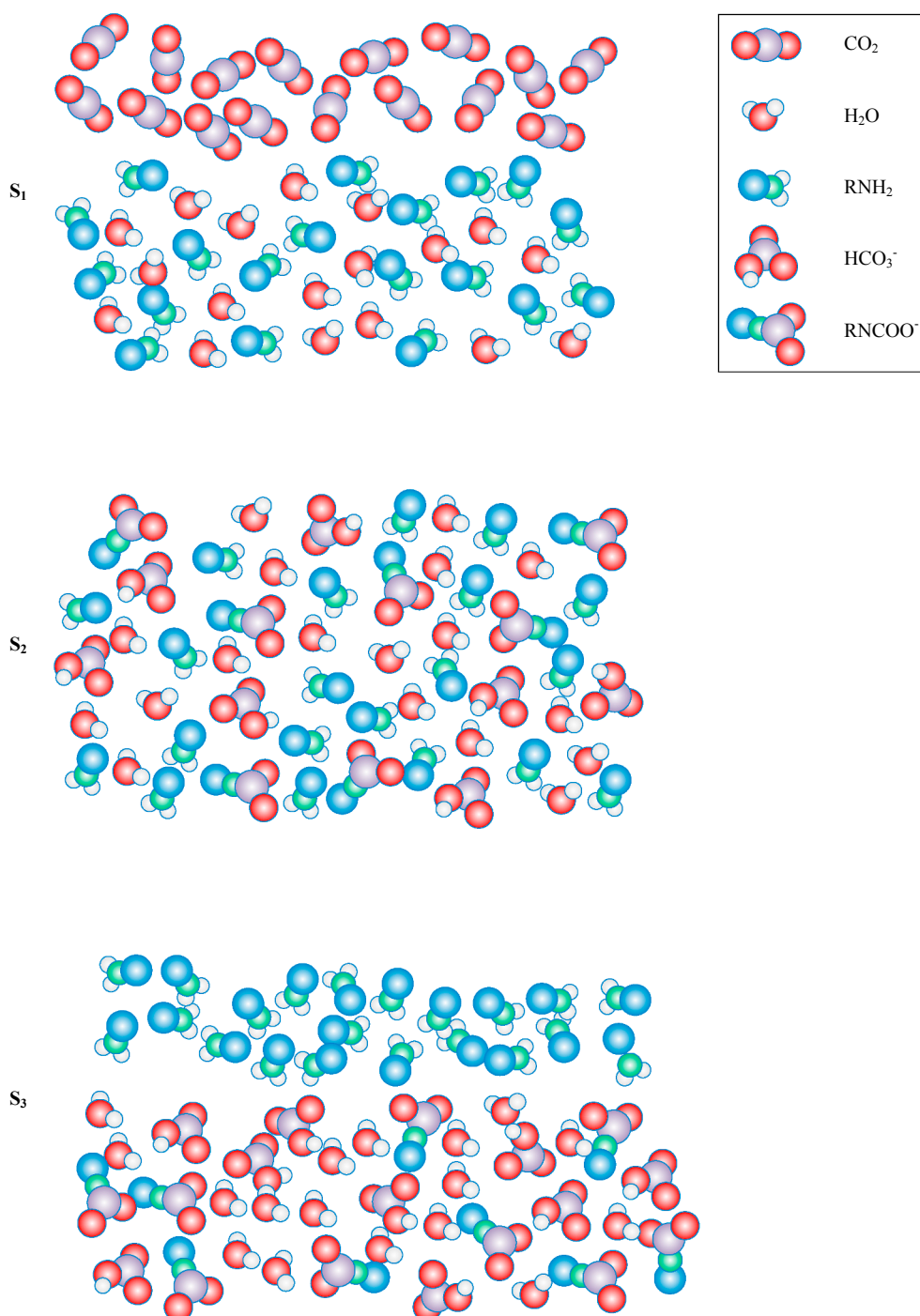


Fig. 3. Phase transition of a neat thermomorphic amine aqueous solution loaded with CO₂ upon the elevation of temperature (note: S₁ = CO₂-lean solution; S₂ = CO₂-rich solution; S₃ = CO₂-rich solution at an elevated temperature).

information on the solvents was not disclosed. In an MEA–isooctanol solvent, the MEA carbamate and protonated MEA were able to bind and form large molecules composed of ionic pairs (MEACOO[−]–MEA⁺), resulting in increases in both density and viscosity and the formation of a new liquid phase (CO₂-rich phase) [67,82]. The species in the resultant CO₂-lean and CO₂-rich phases were analyzed by ¹H and ¹³C NMR. The results revealed that the alcohol was mainly distributed in the CO₂-lean phase, and the protonated amine and its carbamate products were mainly distributed in the CO₂-rich phase [67].

The use of a short-chain alcohol, such as ethanol or 1-propanol, as a solubilizer resulted in a solid–liquid separation upon absorption of CO₂ regardless of the amines used. Unlike with a long-chain alcohol, the

reaction shown in Eq. (8) proceeded in the presence of the short-chain alcohol. In an aminomethyl propanol (AMP)–diethanolamine (DEA)–1-propanol solvent, precipitation occurred after the CO₂ was loaded into the solution. Analysis by solid-state cross-polarization magic angle spinning ¹³C NMR spectroscopy revealed that the precipitates were a mixture of a protonated AMP and its carbamate. The structure of AMP carbamate solids was also confirmed by X-ray diffraction (XRD) analysis [68,69]. However, the AMP carbamate was not detected in the liquid phase. The liquid phase contained the DEA carbamate, 1-propanol carbonate and unreacted alcohol and amines. Sartori and Savage [83] inferred that the precipitation of the AMP carbamate could be due to its low solubility compared with the solubilities of the DEA

Table 1
Summary of nonaqueous biphasic solvents reported in the literature.

Type	Amine	Solubilizers	Split-phase mode	Amine conc. (wt %)	Absorption conditions	CO ₂ loading (mol/mol)	Main species in rich phase	Ref.
Amine–alcohol solvents	MEA	1-Heptanol	Liquid–liquid	10	313 K, 30% CO ₂	0.388	Carbamate	[67]
		1-Octanol				0.375	Carbamate	
		Isooctanol				0.369	Carbamate	
		1-Heptanol	Liquid–liquid	20		0.386	Carbamate	
		1-Octanol				0.381	Carbamate	
		Isooctanol				0.363	Carbamate	
		1-Heptanol	Liquid–liquid	30		0.372	Carbamate	
		1-Octanol				0.383	Carbamate	

^a MMEA is Monomethylethanolamine.

^b DIPA is Diisopropylamine.

^c The upper phase was solids, and the lower phase was liquid.

^d The CO₂ loading was held constant.

carbamate and 1-propanol carbonate and its high lattice energy acquired by ionic interactions in the solid phase, despite its instability in the liquid phase. Note that the AMP carbamate is unstable in solution in the presence of an alcohol because the oxygen in the alcohol triggers a nucleophilic attack at its carbonyl atom, to form an alkyl carbonate and regenerate the amine. Barzagli et al. [68] and Karmee [84] reported that no participation occurred in an AMP solution with a mixture of ethylene glycol and methanol or ethanol as a solubilizer. *N*-Methyl-2-pyrrolidone (NMP) and triethylene glycol dimethyl ether (TEGDME) were also tested as nonaqueous solubilizers for CO₂ absorption into an AMP solution [72], and solid–liquid phase separation occurred.

Solid–liquid phase separation was also observed in MEA–ethanol, DEA–ethanol, triethylenetetramine (TETA)–ethanol and diethylenetriamine (DETA)–ethanol solvents [73,75]. The precipitates were mainly amine carbamates, as indicated by ¹³C NMR and Fourier-transform infrared analyses. In the TETA–ethanol solvent, an alcohol carbonate was also detected in the precipitates. An interesting finding was that the absorption capacities of the tested solvents were much higher than their corresponding aqueous solvents, indicating that the alcohols also served as reactants for CO₂ absorption, as shown in Eq. (8) [73,75]. Alkyl carbonates can be present in either the solid or liquid phase, depending on their solubility in the alcohols [68,73].

For the solvents described above, carbamate molecules were integrated via the hydrogen bonds, such as N–H...O and N–H...N, to form a large molecule. Depending on the molecular weight of the integrated product, either a new liquid phase or a solid phase was formed. For example, in the DETA–ethanol system, a one-dimensional (1-D) ribbon-propagating chain was formed between carbamate molecules via the N–H...O bond. A two-dimensional (2-D) supramolecular network was further formed after the 1-D chains were connected to each other via the intermolecular hydrogen bonds. Finally, a three-dimensional (3-D) carbamate network was formed via van der Waals forces [75].

Most research work on the absorption of CO₂ into alcohol–amine solvents has been focused on phase separation behavior and CO₂ absorption capacity. Only limited information is available on their absorption kinetics and regeneration performance. For solvents containing AMP or TETA, the precipitates were regenerated at relatively low temperatures (e.g., 80–90 °C because of the low decomposition temperatures of their carbamates [69,73]. The rate of CO₂ absorption into the TETA–ethanol solvent doubled that into the TETA–water solution because ethanol not only enhanced the solubility of CO₂ but also facilitated the reaction between TETA and CO₂ [73]. Svensson et al. [71] suggested that to regenerate the amine, the CO₂-rich solids could be used directly without redissolution for CO₂ stripping because the dissolution heat could incur a heat penalty. Overall, the application of amine–alcohol solvents for CO₂ absorption is still in its early stage, and work related to solvent kinetics, stability, resistance to water vapor and cost remains to be conducted. Moreover, dedicated processes tailored to these types of solvents need be researched and developed further.

3.1.1.2. Amino acid–alcohol solvents. Amino acids are regarded as potential solvents for CO₂ capture because they are naturally occurring, are environmentally friendly, exhibit high antioxidation tendencies and have low volatility compared with amines [85–89]. Amino acids react with CO₂ following the same reaction mechanism as alkanol amines. Shen et al. [90] investigated a nonaqueous proline–ethanol solvent for CO₂ capture. Compared with the aqueous proline solution, the proline–ethanol solvent had a higher viscosity (2.0–2.8 times higher) but also showed a greater CO₂ solubility (3.5–3.8 times greater). The absorption rate into the ethanol solvent was increased by 3.5–4.2 times by the addition of 1–2 M potassium proline (ProK). During the absorption of CO₂, the proline–ethanol solvent underwent a liquid–solid phase change, forming a suspension. After a centrifugal separation, two distinct phases appeared: a clear liquid phase at the top and a white solid slurry phase at the bottom. ¹³C NMR and XRD analyses revealed that proline carbamate, bicarbonate and ethyl carbonate salts were the main species in the solid phase. Bicarbonate was present in the solid phase because the solvent contained 0.19–5.97 wt% water, which formed from the neutralization reaction of proline and KOH. However, only 55–60% of the total CO₂ captured was enriched in the solid phase, and the liquid phase still needed to be regenerated. Thus, the solid–liquid system was used directly for CO₂ desorption without a solid–liquid separation. Cyclic absorption–desorption experiments showed that the cyclic CO₂ loading of the proline–ethanol solvent was 3 times the loading of its aqueous counterpart. However, issues associated with ethanol loss resulting from its high volatility and the need for a slurry operation could impose technical challenges. Typically, the rate of CO₂ absorption into an amino acid salt tends to be slower than that into the corresponding amine, which presents another technical challenge to be addressed.

3.1.1.3. Room-temperature ionic liquid and amine blends. Room-temperature ionic liquids (RTIL) have been reported to be thermally stable, be virtually nonvolatile and have a low specific heat capacity, all of which are favorable for CO₂ capture applications [91–94]. In addition, the availability of various combinations of constituent ionic counterparts, may make it possible to tailor an ionic liquid to the required specifications [95]. RTILs can be modified by introducing amino groups to enhance CO₂ absorption [96]. More commonly, alkanolamines and RTIL blends have been investigated as potential alternatives to conventional aqueous amine solvents for CO₂ absorption [74,97,98]. Alkanolamine–RTIL solvents feature the formation of carbamate precipitates upon absorption of the CO₂, which not only helps the solvent reach the stoichiometric CO₂ loading capacity but also provides the opportunity to separate CO₂-bearing products, thereby offering a potential reduction in regeneration energy. Alkanolamine–RTIL solvents hinder the corrosion effect because the absence of an aqueous phase suppresses the formation of oxidizing

Table 2
Summary of aqueous biphasic solvent.

Amine	Split-phase mode	Absorption conditions	CO ₂ loading (mol/mol)	Rich-phase main species	Rich-phase volume ratio	Cyclic loading (mol/mol)	Ref.
5 mol/kg TETA/DMCA (1:4)	Liquid–liquid	303 K, 100% CO ₂	0.614	Carbamate, bicarbonate	0.600		[105]
5 mol/kg DETA/DMCA (1:4)			0.602	Carbamate, bicarbonate	0.680		
5 mol/kg TETA/DEEA (1:4)			0.876	Carbamate, bicarbonate	0.880	0.368	[100]
2 M EEDA/4.5 M DEEA	Liquid–liquid	Temperature at a relatively slow but constant rate, 100% CO ₂	0.56	Carbamate, bicarbonate			
2 M DAB/4 M DEEA	Liquid–liquid		0.6	Carbamate, bicarbonate			
2 M DMBA/4 M DEEA	Liquid–liquid		0.3	Carbamate, bicarbonate			
2 M MAPA/3 M TEA	Liquid–liquid		0.42	Carbamate, bicarbonate			
2.3 M MAPA/2 M DMBA	Liquid–liquid		0.7	Carbamate, bicarbonate			
2 M BDA/4 M DEEA	Liquid–liquid	313 K, 12% CO ₂	0.505	Carbamate, bicarbonate	0.782 ^a	0.31	[101]
2 M BDA/4 M DEEA	Liquid–liquid	313 K, 12% CO ₂	Upper: 0.043 Lower: 0.71	Carbamate, bicarbonate	0.3		[100,106]
Lower phase of 2 M BDA/4 M DEEA							
4.3 M DEEA/2.4 M 2-((2-aminoethyl) amino) ethanol	Liquid–liquid	313 K, 12% CO ₂	0.722	Carbamate, bicarbonate	0.600	0.315	[107]
5 M MAPA/2 M DEEA	Liquid–liquid	313 K, 10% CO ₂	2.5 ^b	Carbamate, bicarbonate	0.649		[109]
1 M MAPA/1 M DEEA	Liquid–liquid	298 K, < 0.4 kPa CO ₂		Carbamate, bicarbonate			[110]
1 M MAPA/2 M DEEA	Liquid–liquid			Carbamate, bicarbonate			
1 M MAPA/3 M DEEA	Liquid–liquid			Carbamate, bicarbonate			
1 M MAPA/5 M DEEA	Liquid–liquid			Carbamate, bicarbonate			
2 M MAPA/1 M DEEA	Liquid–liquid			Carbamate, bicarbonate			
2 M MAPA/3 M DEEA	Liquid–liquid			Carbamate, bicarbonate			
2 M MAPA/4 M DEEA	Liquid–liquid			Carbamate, bicarbonate			
2 M MAPA/5 M DEEA	Liquid–liquid			Carbamate, bicarbonate			
2 M MAPA/5 M DEEA	Liquid–liquid	353 K, ~3 bar CO ₂	0.438	Carbamate, bicarbonate	0.500		[113]
1 M MAPA/5 M DEEA	Liquid–liquid	393 K, ~3 bar CO ₂	0.31	Carbamate, bicarbonate	0.358		
1.92 M taurine	Liquid–liquid	393 K, ~3 bar CO ₂	0.228	Carbamate, bicarbonate	0.329		
	Solid–liquid	298 K, 100% CO ₂	0.5 ^c	Carbamate proline, bicarbonate and ethyl carbonate salts			[117]
2.48 M taurine				Carbamate proline, bicarbonate and ethyl carbonate salts			
2.91 M taurine				Carbamate proline, bicarbonate and ethyl carbonate salts			
3.46 M taurine				Carbamate proline, bicarbonate and ethyl carbonate salts			
2.83 M taurine				Carbamate proline, bicarbonate and ethyl carbonate salts			
2.5 M Alkazid M	Solid–liquid	295 K, 100% CO ₂ ^d	1.0	Carbamate		0.78	[126]
		295 K, 4.7% CO ₂ ^e	0.83	Carbamate			
		295 K, 1.1% CO ₂ ^f	0.7	Carbamate			
2.5 M C ₃ H ₆ NO ₂ K		295 K, 100% CO ₂ ^d	0.9	Carbamate		0.58	
		295 K, 4.7% CO ₂ ^e	0.76	Carbamate			
		295 K, 1.1% CO ₂ ^f	0.66	Carbamate			
2.5 M C ₄ H ₈ NO ₂ K		295 K, 100% CO ₂ ^d	0.96	Carbamate		0.72	
		295 K, 4.7% CO ₂ ^e	0.85	Carbamate			
		295 K, 1.1% CO ₂ ^f	0.6	Carbamate			
2.5 M C ₃ H ₁₀ NO ₂ K		295 K, 100% CO ₂ ^d	0.95	Carbamate		0.63	
		295 K, 4.7% CO ₂ ^e	0.55	Carbamate			
		295 K, 1.1% CO ₂ ^f	0.4	Carbamate			
2.5 M C ₆ H ₁₂ NO ₂ K		295 K, 100% CO ₂ ^d	0.82	Carbamate		0.77	
		295 K, 4.7% CO ₂ ^e	0.38	Carbamate			
		295 K, 1.1% CO ₂ ^f	0.32	Carbamate			

(continued on next page)

Table 2 (continued)

Amine	Split-phase mode	Absorption conditions	CO ₂ loading (mol/mol)	Rich-phase main species	Rich-phase volume ratio	Cyclic loading (mol/mol)	Ref.
2 M potassium taurate	Solid–liquid	298 K, 7.396 kPa CO ₂	0.622	Carbamate proline, bicarbonate and ethyl carbonate salts			[117]
3 M potassium taurate	Solid–liquid	298 K, 1.950 kPa CO ₂	0.547	Carbamate proline, bicarbonate and ethyl carbonate salts			
4 M potassium taurate	Solid–liquid	298 K, 1.241 kPa CO ₂	0.487	Carbamate proline, bicarbonate and ethyl carbonate salts			
4.9 M L-alanine/NaOH	Solid–liquid	313 K, 100% CO ₂	0.9	Carbamate proline, bicarbonate and ethyl carbonate salts		0.62	[87]

^a Weight ratio.

^b The unit is mol CO₂/kg solution.

^c The concentration of amines is 2 M.

^d The experimental time is 200 min.

^e The experimental time is 500 min.

^f The experimental time is 600 min.

species, which are corrosive to the equipment [99].

Larachi and colleagues [74,97,98] investigated a series of DEA–RTIL solvents for CO₂ absorption. DEA was mixed with one of three RTILs, [EMIM][Tf₂N], [BMIM][Tf₂N] and [HMIM][Tf₂N], and all the blends were able to form a solid phase during CO₂ absorption. They observed that the solids formed rose to the surface of the liquid because of the density difference between the solid and liquid phases and the hydrophobicity of the RTILs, which made it easy to separate the solids from the liquid. The addition of Triton X-100, a nonionic surfactant, into the DEA–[HMIM][Tf₂N] solvent prevented the occurrence of a solid phase, indicating that the hydrophobic nature of the ionic liquid played a major role in segregating the solid product. The solid product was identified as a DEA carbamate rather than a bicarbonate or carbonate species on the basis of ¹³C NMR spectra and XRD data. Ionic interactions and intensive hydrogen bonding in carbamate crystals were the major driving forces for carbamate segregation from the RTIL. The precipitation of the carbamate product allowed CO₂ absorption to proceed beyond the equilibrium limitation exerted on a singular liquid phase system.

The kinetics of CO₂ absorption into the DEA–[HMIM][Tf₂N] solvent was investigated by using a laboratory stirred-cell reactor at various amine concentrations, CO₂ partial pressures, agitation speeds and temperatures [98]. A two-scale reaction–diffusion, isothermal, unsteady-state model was developed to describe the CO₂ absorption performance and evaluate its kinetic and mass transfer parameters. The zwitterion mechanism followed by the deprotonation of zwitterions by the amine and the formation of immiscible solid carbamate crystals was assumed to describe the chemical reaction between CO₂ and the solvent. Experimental results showed that the reaction between CO₂ and DEA–[HMIM][Tf₂N] followed third-order kinetics. The values of k_1/k_{R1R2NH} (an indicator of the zwitterion decomposition rate) for the CO₂–DEA–[HMIM][Tf₂N] reaction system were much greater than the literature data for the reaction between CO₂ and DEA dissolved in other organic solvents such as methanol, ethanol, ethyleneglycol, 2-propanol and *n*-butanol [73,100,101]. These results suggests that the zwitterion formed in the DEA–[HMIM][Tf₂N] solvent was much less stable compared with those formed in the DEA–organic solvents. The temperature and agitation speed did not noticeably affect the kinetic constants but did affect the volumetric mass transfer efficiency.

The corrosion rates of carbon steel 1020 in alkanolamine–RTIL solvents were also investigated and compared with those in their counterpart aqueous alkanolamine systems [99,102]. The experimental results revealed that the ionic liquids not only exhibited an excellent corrosion hindrance effect in their neat form but also demonstrated a similar trend in their blends with alkanolamines. Such a beneficial effect was also confirmed in other literature [103]. An energy dispersive X-ray analysis indicated that a protective film was formed on the surface of the steel in the presence of the ionic liquid to shield the metal surface against the detrimental effect of the fluid contents. The main issues related to RTILs are their high cost and high viscosity.

3.1.2. Aqueous biphasic solvents

3.1.2.1. Aqueous amine blends. Amine blends subject to phase separation are generally formulated from two types of amines: one possesses at least one primary (–NH₂) or secondary (–NH) amino group to serve as an absorption accelerator, and the other has a tertiary (–N) amino group to provide the CO₂ loading capacity. Such formulations can exhibit both a rapid absorption rate and large CO₂ uptake [51,104]. Aqueous amine blends are regarded as water switchable solvents. Blending a primary or secondary amine containing multiple protonatable sites (e.g., diamines and triamines), which can increase ionic strength upon loading of the CO₂, and a tertiary amine with suitable hydrophobicity tends to facilitate the formation of two phases.

Many aqueous amine blends have been reported in the literature in recent years, as shown in Table 2 [100,105–107]. Svendsen and colleagues [108,109] investigated an aqueous blend of *N*-methyl-1,3-

propane-diamine (MAPA) and 2-(diethylamino)-ethanol (DEEA). Wang et al. [101] investigated a blend of 1,4-butanediamine (BDA) and DEEA for CO₂ absorption. MAPA and BDA are isomers and primary diamines, whereas DEEA is a tertiary amine containing an alcohol hydroxyl. Upon CO₂ absorption, both the MAPA–DEEA and BDA–DEEA solvents transformed into two liquid phases, and more than 95% of the captured CO₂ was enriched in the lower liquid phases. The authors confirmed that the liquid–liquid transition was due to the fast reaction rate of the primary diamines with CO₂ and the limited solubility of their carbamate products in DEEA. Liquid chromatography-mass spectrometry and quantitative ¹³C NMR analyses revealed that MAPA (or BDA) and DEEA were present in both the lower and upper phases. The presence of DEEA dominated in the upper phase, whereas the MAPA [or dibutylamine (DBA)] and its carbamate product dominated in the lower phase. The main species in the lower phase consisted of the primary and secondary carbamate products (including dicarbamates), protonated amines and bicarbonate or carbonate. The upper phase served as a buffer for DEEA, which was able to transfer to the lower phase as more CO₂ was captured by the solvent. As a result, the volume of the lower phase and the ratio of DEEA to MAPA (or BDA) in the lower phase increased with increasing CO₂ loading [108]. This result also indicates that the dual phases formed might transform to a homogeneous phase again with a further increase in CO₂ loading [108,109]. In other words, a tradeoff between the amount of CO₂ loaded and the maintenance of dual liquid phases might need to be considered. The phase separation was accelerated at higher absorption temperatures [109].

The compositions of the MAPA–DEEA and BDA–DEEA blends were optimized to achieve a high cyclic capacity [101,106,110]. Solutions of 2 M DBA mixed with 4 M DEEA and 2 M MAPA with 5 M DEEA showed the best performance. For example, the BDA–DEEA blend exhibited a 48% higher cyclic capacity compared with that for the 5 M MEA solution. Even at a high CO₂ loading level (e.g., ~0.45 mol/mol of amine), free BDA molecules were also detected in the lower phase, indicating that the BDA carbamate was regenerated by DEEA based on a shuttle mechanism. The kinetics of CO₂ absorption into the MAPA–DEEA and BDA–DEEA blends was investigated by use of a string of discs contactor and a wetted wall column, respectively, at temperatures ranging from 25 to 65 °C under CO₂ partial pressures less than 0.4 kPa or ranging from 3 to 35 kPa [101,106,110]. The termolecular mechanism proposed by Crooks and Donellan [111] and further investigated by da Silva and Svendsen [112] was used to describe the CO₂ reaction with the primary amine MAPA or BDA in the blend. They concluded that the reaction between the primary amine and CO₂ occurred in a single step and was termolecular and that the overall mechanism of CO₂ absorption could be regarded as a reaction between CO₂ and DEEA in parallel with a reaction of CO₂ with MAPA or BDA. In the BDA–DEEA blend, the concentration of BDA strongly affected the rate of CO₂ absorption. A kinetic model based on the two-film theory, the pseudo-first-order reaction assumption and the DEEA clustering hypothesis was developed to interpret the mass transfer and absorption behavior of CO₂ absorption into the MAPA–DEEA blend [110]. The clustering hypothesis has been confirmed in the literature, as evidenced by the solubility and kinetic data of the DEEA aqueous solution [28]. According to this hypothesis, clusters of DEEA form in the aqueous solution via intermolecular hydrogen bonding between the atoms of N and O in two different DEEA molecules, and they grow larger with increasing temperature and DEEA concentration. The formation of large clusters can favor CO₂ solubility because this creates the space required for CO₂ to coordinate into clusters, resulting in a high mass transfer rate and fast kinetics.

Furthermore, the values of heat of absorption for 5 M DEEA, 2 M MAPA, 1 M MAPA, 2 M MAPA + 5 M DEEA and 1 M MAPA + 5 M DEEA in approximately 3 bar of pure CO₂ and at 40, 80 or 120 °C were determined by use of a reaction calorimeter [113]. Experimental results showed that the heat of absorption depended on the CO₂ loading, temperature and composition of the solvent. Compared with the

benchmark 5 M MEA, 2 M MAPA + 5 M DEEA showed a slightly higher heat of absorption and 1 M MAPA + 5 M DEEA showed a comparable absorption heat at 40 °C at lower CO₂ loadings (i.e., less than ~0.2 mol of CO₂/mol of amine). However, the heat of absorption decreased rapidly with increasing CO₂ loading. The MAPA–DEEA blends showed high loading capacities compared with 5 M MEA at 40 °C. It was also observed that 1 M MAPA + 5 M DEEA became one liquid phase when the CO₂ loading exceeded 0.23 mol of CO₂/mol of amine. Furthermore, experiments of CO₂ desorption from the rich-phase solution showed that the MAPA–DEEA solvent achieved a higher CO₂ stripping pressure at low temperatures (e.g., less than 100 °C) compared with the benchmark 5 M MEA solvent [113,114], indicating that the temperature of steam heat usage and the CO₂ compression work required could be reduced.

Lu and colleagues [105] screened approximately 50 amine-based aqueous solvent blends, each of which consisted of a primary or secondary monoamine or polyamine as an absorption accelerator and *N,N*-dimethylcyclohexylamine (DMCA) or DEEA as a regeneration promoter. Rates of CO₂ absorption and phase transition behavior were evaluated at 30 °C, and phase equilibrium behavior of CO₂ desorption was evaluated at 80 °C for these solvents by use of laboratory batch reactors. The experimentally measured solvent performance was correlated with several important structural factors, such as the length of the alkyl chain, the numeric ratio of N to C atoms and the molecular conformation (e.g., linear, branched, cyclic or heterocyclic) of the amine component. The solvent blends containing larger molecules of amines (e.g., C > 8) showed relatively slower absorption rates and tended to form gel-like solids, which were insoluble up to 60 °C (e.g., dicyclohexylamine and dihexylamine). When used as an absorption accelerator, the linear amines exhibited superior absorption performance compared with cyclic amines with the same number of C atoms. The solvent blends containing either DMCA or DEEA as a regeneration promoter did not affect the relationship between the absorption performance and the structure of the amine accelerator, indicating that the performance of CO₂ absorption mainly depended on the selection of the absorption accelerator. In addition, the phase transition behavior was affected by the molar ratio and the total concentration of the amine blends because of variations in their relative partitions into the two individual liquid phases. Overall, the screening results suggested that the biphasic solvents with an amine accelerator containing 3–4 N and 4–6 C atoms generally exhibited more favorable absorption and desorption performance without the potential operational concerns.

On the basis of the above research, DETA (C₄H₁₃N₃) was further studied as an amine accelerator [34]. DETA was blended with the tertiary amine pentamethyldiethylenetriamine (PMDETA, C₉H₂₃N₃). PMDETA, which contains three tertiary amino groups, was used to provide a high CO₂ loading capacity. A phase transition to two liquid phases occurred as the CO₂ loading to the DETA–PMDETA blend reached 0.2 mol mol^{−1}. Like the MAPA–DEEA and DBA–DEEA solvent blends, the rich-phase volume of the DETA–PMDETA blend increased with increasing CO₂ loading. The dual phases remained even at a high CO₂ loading (i.e., ~0.8 mol mol^{−1}), primarily because of the high hydrophobicity of PMDETA. Compared with the benchmark 5 M MEA, the DETA–PMDETA solvents achieved an approximately 35% higher CO₂ loading capacity. Note that the rich-phase volume and the total CO₂ loading capacity of the solvent blend increased with increasing DETA concentration because of the resultant increasing hydrophilicity. To identify the CO₂ absorption and desorption mechanisms for the DETA–PMDETA blend, detailed species of several CO₂ lean- and rich-phase samples obtained at different CO₂ loadings, simulating the various absorption and desorption conditions, were analyzed by ¹H, ¹³C and 2-D NMR [34]. As shown in Fig. 4, DETA (panel A) reacted with CO₂ before PMDETA (panel B) because of its high reaction rate. Once a certain amount of CO₂ was loaded, dual liquid phases were formed. Because of the limited solubility of PMDETA in water, it was dominant in the upper phase (CO₂-lean phase). Before molecular DETA was consumed by the

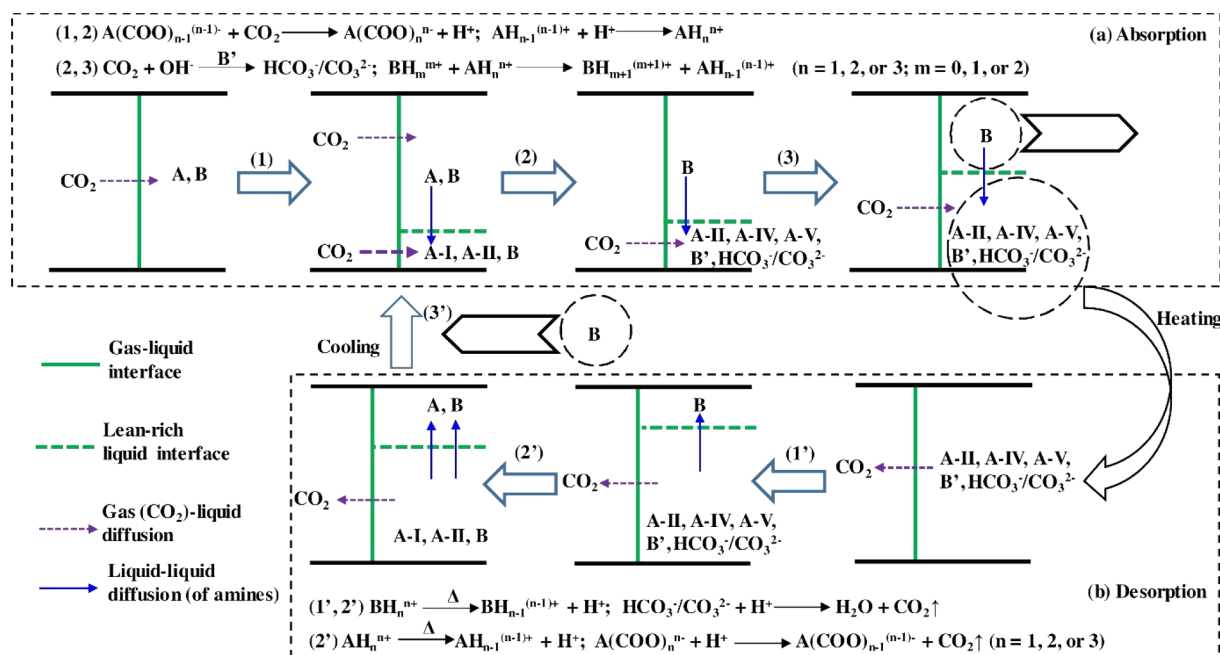


Fig. 4. Mechanisms of the closed loop of (a) CO₂ absorption into the biphasic blend of DETA and PMDETA and (b) CO₂ desorption from its CO₂-rich phase. The green solid and dashed lines denote the gas-liquid and lean-rich liquid interfaces, respectively. The purple dashed arrows denote the mass transfer of CO₂ from a gas to liquid phase or the opposite, whereas the blue arrows denote the diffusion of amines A and B from one liquid phase to the other. All the block arrows denote the stages between two characteristic system states. A, B, A-I, A-II, A-III, A-IV and A-V, and B' denote molecular DETA, molecular PMDETA, species of different A groups, and species of group B, respectively [34]. Reproduced from ref. 34 with permission from Elsevier.

reaction with CO₂ in the lower phase (CO₂-rich phase), the volume of the lower phase did not vary significantly, and PMDETA did not noticeably transfer from the upper to the lower phase. When molecular DETA was depleted, the reaction between CO₂ and PMDETA became dominant and a large amount of PMDETA transferred from the lean phase to the rich phase to sustain the CO₂ absorption, resulting in a rapid volumetric expansion of the rich phase and the formation of HCO₃[−]/CO₃^{2−}. This absorption mechanism was consistent with the work described above. During the CO₂ desorption from the rich-phase solvent (Fig. 4), PMDETA was regenerated earlier than DETA because CO₂ was less strongly affiliated with PMDETA than DETA. Because of the limited aqueous solubility of PMDETA molecules, the regenerated PMDETA was immiscible with the parent solvent, which could again cause the formation of dual liquid phases. As a result, the volume of the upper-phase liquid gradually expanded as the desorption proceeded. In addition, the stripping pressure over the DETA–PMDETA rich-phase solvent was twice that of the benchmark 5 M MEA solution at the same temperature (120 °C).

According to the absorption mechanism elucidated above, the phase transition behavior is affected by the aqueous solubility of the tertiary amine. Because DEEA is more hydrophilic than PMDETA, the rich-phase volume of the DETA–DEEA solvent is much larger than that of the DETA–PMDETA solvent [115]. Kinetic analysis of CO₂ absorption into the DETA–DEEA solvent using a wetted wall column reactor showed that the liquid-side mass transfer resistance accounted for 68.3–83.5%, depending on the CO₂ loading of the solvent, indicating that the absorption rate was limited by the liquid-side mass transfer. As a result, increasing the DETA concentration to greater than 1 M could further accelerate the absorption rate. Furthermore, a biphasic solvent was formulated by blending the two tertiary amines *N,N*-dimethylbutylamine and DEEA. The solvent exhibited a good CO₂ absorption capacity and a potentially low heat duty, but the absorption rate was slow [116].

3.1.2.2. Aqueous amino acid salt solutions. Aqueous amino acid salt solutions can undergo a phase transition during CO₂ absorption. Various types of amino acid salts, including linear amino acid salts

(e.g., glycine, taurine, sarcosine, β-alanine and γ-aminobutyric acid), sterically hindered amino acid salts (e.g., alanine, α-aminobutyric acid, α-methyl ananine, serine and cysteine), cyclic amino acid salts (e.g., proline, 4-hydroxy proline and pyroglutamic acid) and polyamino acid salts (e.g., asparagine, glutamine, diglycine and arginine) were investigated for this application [117–125]. CO₂ absorption into amino acid salt solutions followed a reaction mechanism similar to that for the nonaqueous amine blends described above. Reaction products precipitated out with the concentrated solutions, at high CO₂ loadings, or both because of the formation of amino acid zwitterion-carbonate or bicarbonate complexes and the salting-out effect [117,126,127]. Kumar and colleagues [117,127] reported that in a highly concentrated amino acid salt (> 3 M), the precipitation of reaction products occurred at an even lower CO₂ loading. Typically, the reaction of CO₂ with an amino acid salt containing a primary or secondary amino functional group forms a protonated amine and a carbamate, which undergoes further hydrolysis to form the bicarbonate or carbonate salt. An amino acid with high alkalinity (*pK_a*) may promote hydrolysis of the carbamate. In addition, the substituent ligand attached to the α-carbon (the carbon atom adjacent to an amino group) in an amino acid salt makes the carbamate less stable and hence facilitates hydrolysis of the carbamate [126,128]. Therefore, precipitates are composed of the carbonate of an amino acid zwitterion, the amino acid zwitterion, a bicarbonate and a mixture of the amino acid zwitterion and the bicarbonate, depending on both the structure and *pK_a* of the amino acid salt [117,124,126,129]. Generally, primary amino acids result in amino acid zwitterion precipitates, whereas hindered amino acids result in a mixture of bicarbonate and amino acid zwitterion precipitates. Majchrowicz et al. [129] investigated the critical point at which the precipitates began to form during CO₂ absorption under various operational conditions, such as various temperatures, amino acid concentrations, types of counterions and CO₂ partial pressures. They confirmed that (1) higher solubility limits could be attained for an amino acid salt under higher temperatures and lower CO₂ partial pressures, (2) precipitation could occur at lower CO₂ partial pressures with higher amino acid concentrations and (3) the

solubility limit of an amino acid salt depended on its counterion following the order of $K > Na > Li$. The precipitation of reaction products increased the equilibrium CO_2 loading capacity according to Le Chatelier's principle. However, it could also increase plugging and fouling risks in absorbers and heat exchangers.

Kumar et al. [117] found that the presence of solids in the liquid phase reduced the volumetric mass transfer coefficient ($k_L a$) of the gas–liquid contactor during the absorption of N_2O gas into a slurry. The effect of solids on the gas–liquid mass transfer has been intensively investigated. In general, the gas–liquid mass transfer coefficient was enhanced if solid particles had any physical or chemical interaction with gas species. In the absence of a physical or chemical interaction between the gas and the solid, mass transfer was not affected or adversely affected [130,131]. Because N_2O is inert, the observed decrease in $k_L a$ has been ascribed to a decrease in the effective interfacial area (a) and an increase in liquid viscosity in the presence of solid particles. In contrast, the presence of solids in a solution that physically or chemically interacted with CO_2 enhanced the gas–liquid mass transfer in the CO_2 absorption system [131]. Kumar et al. [117] assessed the effect of solid particles on the vapor–liquid equilibrium (VLE) behavior of a CO_2 -laden amino acid salt [potassium taurate (TAU)] by comparing the experimental data with the VLE modeling predictions obtained for a system without precipitates. The comparison revealed that the presence of solid particles significantly reduced the equilibrium CO_2 partial pressure under the same CO_2 loading, which resulted in a higher mass transfer driving force and greater CO_2 capacity.

3.2. Thermomorphic solvents

3.2.1. Lipophilic amine solvents

Lipophilic amines are partially miscible with water, and their aqueous solutions may be thermally induced to encounter a liquid–liquid phase transition. The CO_2 -laden liquid phase may be regenerated at relatively low temperatures (e.g., 60–90 °C), which allows the CO_2 to be stripped off by low-quality steam or even waste heat. The lean lipophilic amine solvent can be either homogeneous or heterogeneous. Upon absorption of CO_2 , the solvent remains homogeneous or transforms into a homogeneous phase. When heated to a higher temperature (60–90 °C), the CO_2 -loaded solvent transforms into two liquid phases, and the rich phase is regenerated within the same temperature range. To enable solvent regeneration at relatively low temperatures (60–90 °C), the LCST of lipophilic amines should fall within this temperature range. In addition to the LCST, the absorption rate, capacity, regeneration efficiency, thermal and oxidative stability, solvent expense and environmental impact were also taken into account when screening lipophilic amines [60].

On the basis of the above screening criteria, a class of lipophilic amine blends were identified that could combine the advantages of different types of amines (Table 3) [60,132–135]. Generally, a primary or secondary lipophilic amine was adopted as an activator to enhance the absorption rate, and a tertiary lipophilic amine was adopted as a promoter to provide a high loading capacity [132,136]. The mechanism of CO_2 absorption into this class of solvents was similar to that of the aqueous amine blends described above. The LCST of the solvent was tunable by changing the amine type, concentration and composition [132]. A mixture of the secondary amine dipropylamine (DPA) and the tertiary amine DMCA resulted in a thermomorphic solvent [60]. Experimental results showed that the desorption of CO_2 was greatly enhanced by the liquid–liquid phase transition. A thermodynamic analysis using the method developed by Hasse-Stuttgart revealed that the steam required to regenerate the DPA–DMCA solvent at 70 °C was 30% less than that for the benchmark 5 M MEA. Moreover, the minimum solvent required to achieve the same removal efficiency was approximately 35% less than that of the 5 M MEA. The DPA–DMCA solvent was also reported to exhibit good thermal and oxidative stabilities because of the low regeneration temperature adopted. However, there were concerns

about the slow rate of the CO_2 absorption reaction with DMCA and the potential precipitation of protonated DPA ions and bicarbonates [133,137].

An alkylamine, initially undisclosed [131,133,134] and later disclosed as *N*-methylcyclohexylamine (MCA), a secondary amine [63,138], was used to replace DPA as a rate activator. The new solvent, named MCA–DMCA, with a 1:1 M ratio of MCA to DMCA and a total amine concentration of 4 M, exhibited a high absorption rate, which was comparable with that of an MCA neat solution, and had promising regenerability, similar to that of DMCA [133]. The performance of the MCA–DMCA solvent, in terms of either net loading capacity (up to 3.34 mol/L at 30 °C) or regeneration efficiency (up to 98% of the total CO_2 at 80 °C), appeared to be noticeably superior to that of the conventional alkanolamines. However, the MCA–DMCA solvent had issues associated with foaming and water and amine evaporation [132]. Therefore, a foam breaker, downstream condenser or water scrubber was regarded as necessary to overcome these problems, which could complicate the process. Another concern was operational, given that the solution was heterogeneous during CO_2 absorption because of its relatively low LCST. To elevate the LCST of MCA–DMCA, an aqueous solubilizer such as AMP was used to regulate the phase transition behavior [134]. The addition of AMP (9 wt%) elevated the LCST of MCA–DMCA by 15–25 °C, depending on the total concentration and the composition of the MCA–DMCA solvent [134,138]. For instance, at a 3:1:1 DMCA/MCA/AMP ratio, the LCST of the blend reached greater than 40 °C, which is in compliance with the typical temperature of the absorption process. The absorption or desorption performance was not significantly affected when the amount of AMP was less than 10 wt%. When 20 wt% of AMP was added to MCA–DMCA, the regenerability deteriorated considerably [134].

It was further reported that during solvent regeneration, the organic (upper) phase containing the free lipophilic amine acted as an extractive agent. The organic phase extracted the regenerated amine from the aqueous (lower) phase, hence favorably driving the reaction toward the dissociation of carbamate and bicarbonate species according to Le Chatelier's principle [63]. To promote CO_2 desorption from the lipophilic amine solvent blend, various inert hydrophobic organic compounds, such as pentane, hexane, cyclohexane and isohexane, were used as extractive agents. Such extractive regeneration was intended to reduce the temperature of CO_2 desorption to 40–70 °C and intensify the solvent recovery process. Through multiple stages of extraction, more than 90% of the absorbed CO_2 could be released [44,139]. However, an additional distillation process was required to recover the inert extractive organic compound, which would increase the cost of CO_2 capture.

3.2.2. DMX solvents

IFP Energies nouvelles has developed a series of DMX™ solvents [46,135]. Compared with other thermomorphic solvents, DMX solvents show a higher LCST, thus incurring phase transitions at a higher temperature. The DMX solvents have been reported to absorb CO_2 at 40 °C, after which the CO_2 -laden solvent is heated to 90 °C to induce a liquid–liquid phase transition [135]. The compositions of DMX solvents are proprietary. One of DMX solvents, DMX-1, has been described as a blend of a tertiary amine with a low LCST and a primary or secondary amine with a high LCST. DMX-1 has been reported to exhibit a CO_2 absorption capacity comparable with that of the MEA solvent but with a cyclic capacity twice that of MEA. The absorption heat of DMX-1 was estimated from the VLE data by using the van't Hoff law and found to be 29.4% lower than that of MEA [135]. Thermal stability tests indicated that DMX-1 was more stable than MDEA, which is regarded as a stable solvent for natural gas treatment. For example, no degradation of the solvent occurred at temperatures up to 160 °C [140,141]. The researchers suggested, based on the studies above, that the DMX-1 solvent had a high cyclic capacity, less stripping energy use, low absorption heat, better thermal stability, and a reduced mass of solvent required

Table 3
Summary of thermomorph biphasic solvents.

Type	Amine	Split-phase mode	Amine conc. (wt %)	Absorption conditions	CO ₂ loading (mol/mol)	Absorption rate (mol/L s)	Main species in rich phase	Cyclic capacity (mol/L of solution)	Cyclic loading (mol/mol)	Regenerability (%)	Ref.
Lipophilic amine solvents	3 M DPA /DMCA (1:2)	Liquid–liquid	30	313 K, 25% CO ₂	1.014	0.000707	Carbamate, bicarbonate	2.0			[60]
	0.75 M DPA /2.25 M DMCA	Liquid–liquid		313 K, 4–100 kPa CO ₂	0.682	0.000562 ^a	Carbamate, bicarbonate				[132]
	0.75 M MEA /2.25 M MDEA				0.47	0.000297 ^a	Carbamate, bicarbonate		0.197		
	0.75 M MCA /2.25 M DMCA	Liquid–liquid	39.6	303 K, 19.4% CO ₂	0.89	0.000593 ^a	Carbamate, bicarbonate	2.61	0.606	98.1	[133]
	1.5 M MCA /1.5 M DMCA		38.3		0.96		Carbamate, bicarbonate	2.81		97.2	
	2 M MCA /2 M DMCA		52.1		0.85		Carbamate, bicarbonate	3.34		98	
	0.75 M MCA /2.25 M DsBA ^b	Liquid–liquid		303 K, 19.4% CO ₂	0.78		Carbamate, bicarbonate			99.2	[134]
	0.75 M MCA /2.25 M EDP				0.88		Carbamate, bicarbonate			97.3	
	2 M MCA /2 M DMCA /9% AMP				0.95		Carbamate, bicarbonate	3.4			
	Molecule B	Liquid–liquid	30	313 K, 100% CO ₂	2.8 ^c		Carbamate	2.1 ^d			[135]
DMX [™] solvents	Molecule D		30		2.4 ^c		Carbamate	1.2 ^d			
			50		3.2 ^c		Carbamate	2.1 ^d			

^a The CO₂ loading is 0.2 mol/mol.

^b DsBA is Diisobutylamine.

^c The unit is mol kg⁻¹ of solution.

^d The unit is mol L⁻¹ of solution.

for regeneration, thus resulting in significant savings in energy usage.

4. Development of phase transitional CO₂ absorption processes

Several CO₂ absorption processes using different phase change solvents have been proposed. These include a “self-concentration” process, the iCap process, the DMX process, the TBS system and the DECAB process (Table 4). Most of these processes, except the self-concentration process, are enabled by aqueous solvents.

4.1. Self-concentration process by the 3H Company

The self-concentration process uses a nonaqueous solvent that is an amine and alcohol blend. CO₂ absorption operates at 35 °C and the fresh homogeneous solvent transforms into two liquid phases upon loading of CO₂ [80,142]. The rich phase (lower phase) is separated in the decanter, after which it enters the cross-heat exchanger and then flows to the stripper for solvent regeneration at 115–125 °C. The regenerated solvent from the stripper is mixed with the lean (upper) phase from the decanter, and the solvent mixture is then returned to the absorber for CO₂ absorption. The developers estimated that the process, which uses a proprietary 3H-1 solvent, could reduce the heat duty required for solvent regeneration by 72.3% compared with the benchmark 5 M MEA [142]. However, details of the heat duty estimation are not available, and the reported energy savings could not be validated. This process is in a conceptual stage, and the present status of process development is unknown.

4.2. iCap process by the Norwegian University of Science and Technology

The iCap process developed by the Norwegian University of Science and Technology, uses a phase transitional aqueous solution, a blend of MAPA (2 M) and DEEA (5 M) [143]. Like the self-concentration process, the liquid–liquid phase transition is intrigued upon CO₂ absorption, and only the rich-phase liquid is sent to the stripper for regeneration. In addition, the CO₂-concentrated rich phase allows a high stripping pressure in the stripper and thereby lowers the required stripping heat. After intensive laboratory work on the thermal stability, kinetics, absorption capacity and desorption performance of the solvent, pilot testing to treat approximately 90 m³ h^{−1} of flue gas was conducted for 4 months [143]. The absorber was 0.15 m in diameter and 4.23 m in packing height. The stripper was 0.1 m in diameter and 3.57 m in packing height. Both columns were packed with a gauze packing (Mellapak BX), with a nominal specific area of 500 m² m^{−2}. During the pilot campaign, CO₂ absorption operated at 51 to 63 °C and CO₂ stripping operated at 107–117 °C. The feasibility of the iCap process was demonstrated, and no operational issues related to high solvent viscosity and foaming were observed. For the MAPA–DEEA rich-phase liquid with a CO₂ loading of 0.9–1.1 mol/mol of MAPA, the specific reboiler duty (defined as the reboiler power use per unit mass of CO₂ desorbed) was 2.2–2.4 GJ/tonne of CO₂. Compared with the MEA process (heat duty of 3.7 GJ/tonne of CO₂), significant energy savings were achieved by the iCap process. A process model, CO₂SIM, was developed by this group to simulate the iCap process. The model was validated by the experimental data obtained at the pilot plant. The volatility of the MAPA–DEEA solvent may not be insignificant, especially when the absorption temperature is elevated by the heat released from CO₂ absorption. The volatility concern associated with this solvent needs to be further assessed and addressed.

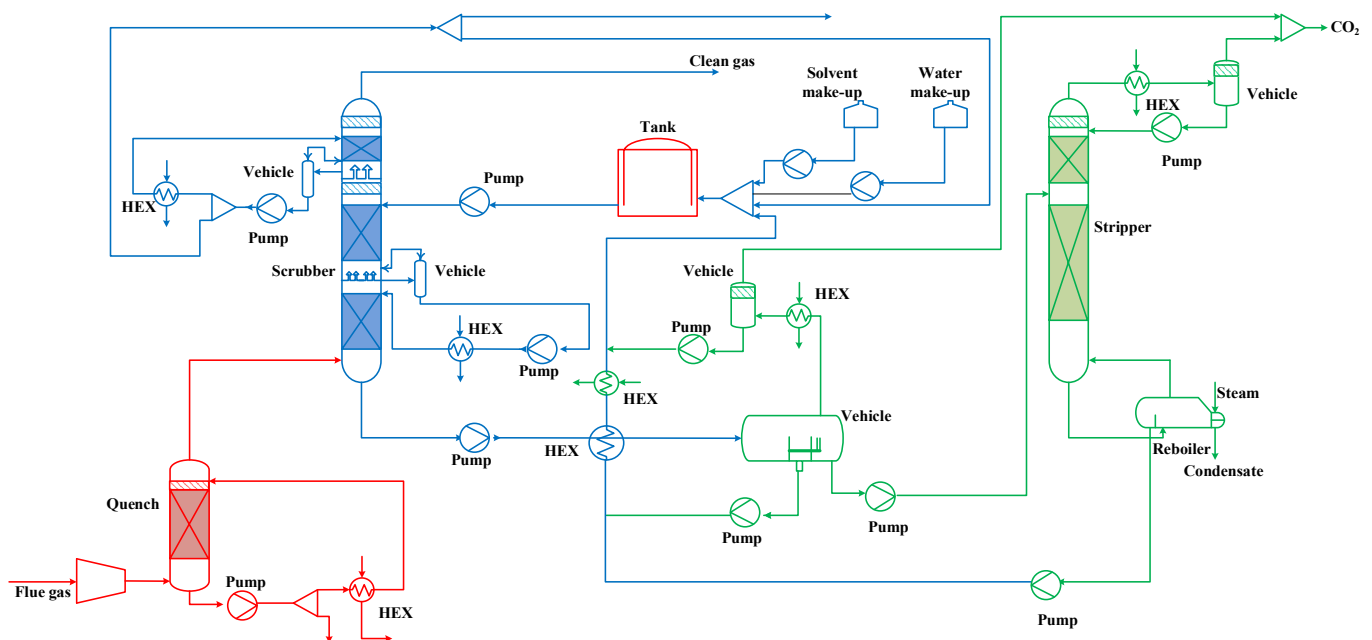
4.3. DMX process by IFP Energies nouvelles

The DMX process based on aqueous DMX solvents has been under development by IFP Energies nouvelles (see Fig. 5) [46,140,144]. As mentioned above, the DMX solvent loaded with CO₂ is able to form two immiscible liquid phases at an elevated temperature. Unlike the self-

Table 4
Summary of processes in development based on biphasic solvents.

Process	Vendor	Solvent	Phase separation method & conditions	Solvent regeneration method & conditions	Energy use (GJ/t of CO ₂)	Development stage	Comments (advantages/disadvantages & challenges)	Ref.
MEA process “Self-concentration” process	3H Company	MEA, DEA in 1-octanol, heptanol, 1-octanol, isooctanol and water	Increased loading of CO ₂ in 35 °C and alcohol solvent	100 °C	3.4–3.7	Scale-up batch	Reduce the heat duty required for solvent regeneration by 72.3% compared with the benchmark 5 M MEA	[46,143,157]
iCap process	Norwegian University of Science and Technology	DEEA/MAPA	Increased loading of CO ₂ in 51–63 °C	107–117 °C	2.2–2.4	Pilot test	A significant energy saving but a higher volatility compared with MEA	[142]
DMXTM process	IFP Energies nouvelles	DMX-A™ solvent	Elevated temperature	~90 °C	2.3	Mini-pilot test	Reduce the energy consumption and the operational expenditures	[143]
		DMX™ solvents		80 °C	< 2.5	Mini-pilot test	Higher cyclic capacity; low degradation and corrosive; controllable cost; lower energy consumption	[45,144]
TBS system	IFP energies nouvelles	DMCA/MCA/AMP	Increased loading of CO ₂ in 40 °C	80 °C ^a	3.5	Pilot test	Small equipment needed and slightly reduce the energy consumption but relatively high volatility and high viscosity of CO ₂ -rich phase	[140]
DECAB Plus process	Netherlands Organization for Applied Scientific Research, University of Twente, Delft University of Technology.	Potassium taurate	Increased loading of CO ₂ in 40 °C	120–130 °C.	2.4	Concept	Low energy consumption of reboiler. However, the DECAB Plus process required an additional ~ 0.96 GJ/tonne of CO ₂ heat to redissolve the precipitates, resulting in a high energy consumption for the entire process.	[44,139]
								[124,145]

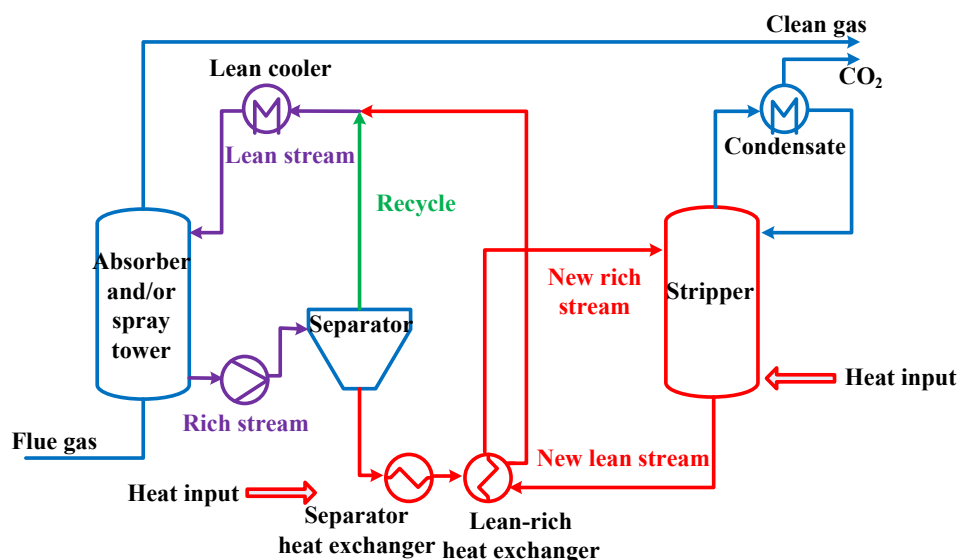
^a Solvent regeneration by using the lean phase as an extractive agent, agitation, ultrasound mixing, nucleation, or multi-stage extraction.



concentration and iCap processes, the decanter (*i.e.*, phase separator) in the DMX process is located downstream of the cross-heat exchanger (Fig. 5). The lean phase formed in the decanter is sent directly back to the absorber, and the rich phase is injected into the stripper for solvent regeneration. The CO₂ stripping operates at approximately 90 °C [46]. A process simulation study was conducted for CO₂ capture from a 630 MWe circulating fluidized bed coal-fired power plant by use of SimSci PRO/II software with a proprietary thermodynamic model created by IFP Energies nouvelles. The results revealed that the DMX process based on the DMX-1 solvent was able to reduce the reboiler heat duty to 2.3 GJ/t of CO₂ [45,46]. Raynal et al. [45,46] also claimed that the reboiler heat duty could be further reduced to 2.1 GJ/t of CO₂ with a dedicated process scheme with heat integration. A techno-economic analysis showed that the capital expenditure (CAPEX) of the DMX process was comparable with that of the benchmark MEA process but that the operational expenditure (OPEX) was 35% lower.

The DMX process has been tested in a mini-pilot plant with 1500 h

of 24/7 operation [144]. During the tests, the operability of the process, particularly the use of a decanter downstream of the cross-heat exchanger, and the long-term effects of equipment corrosion, solvent degradation and emissions were investigated. The results of the mini-pilot test without heat integration showed that the reboiler heat duty amounted to 2.5 GJ/t of CO₂, which is comparable with the process simulation results. The mini-pilot test indicated that the technology could be further scaled up with a low risk. The techno-economic analysis also revealed that the DMX process with a higher stripping pressure could result in lower electricity and steam consumption. In the high-pressure stripping scenario (6.6 bar), the CO₂ avoidance cost was estimated at 42.6 €/tonne of CO₂ avoided compared with 56.5 €/tonne of CO₂ avoided for the MEA process [140]. Because the CAPEX of the DMX process is high, similar to the MEA process, further efforts need to be expended on process design and optimization to reduce the CAPEX and achieve the best tradeoff between the CAPEX and OPEX [45].



4.4. TBS system by the University of Dortmund

An aqueous solvent blend of DMCA, MCA and AMP (3:1:1 with a total amine concentration of 5 M) was selected based on solvent screening studies for application in a TBS CO₂ absorption system [63]. In the TBS system, the CO₂ absorption process operates at 40 °C, and the CO₂ stripping process operates at 80 °C [139]. In this system, the organic compounds (CO₂-free amines) in the lean phase act as extractive agents to extract the regenerated amines into the lean phase, thus facilitating the regeneration of the rich-phase solvent. The rich-phase solvent is regenerated with steam stripping and enhanced by the self-extraction. However, the rate of the self-extraction operation is slow. Therefore, additional steps, such as agitation, ultrasound mixing, nucleation and multi-stage extraction using an inert extractive agent, may be needed. A TBS system with a multi-stage extractive regeneration step has been proposed. The system includes an absorber, a phase separation unit, a four-stage extraction unit (using an inert agent such as pentane) and a vapor recovery unit. The energy use required by the TBS process was estimated to be approximately 3.5 GJ/t of CO₂, 30% of which was consumed by the distillation separation of the inert extractive agent from the lean phase [44]. As a result, the overall heat usage of the TBS process was comparable with that of the benchmark MEA process. However, because low-quality steam (~80 °C) is used in the TBS system compared with that (~120 °C) in the MEA process, the TBS system could slightly reduce the parasitic power loss compared with the MEA process.

4.5. DECAB plus process by process Monkey Ltd.

Fig. 6 [124] shows a schematic diagram of the DECAB Plus process developed by Process Monkey Ltd. The process uses an aqueous amino acid salt (e.g., TAU) as a solvent for CO₂ capture [124,145]. CO₂ absorption operates at 40 °C, and solid precipitates occur with the loading of CO₂. The resultant slurry flows to a solid–liquid separator, where the supernatant is partially removed to obtain a new slurry with a concentrated CO₂ loading. The separated supernatant returns to the absorber, and its fraction in the total mass flow to the separator is referred to as the recycle split fraction (RSF). The new slurry is preheated, resulting in redissolution of the precipitates and thus lowering the pH value of the solution, which can facilitate the release of the chemically bound CO₂ during CO₂ stripping. The preheated slurry is then sent to the stripper for regeneration at 120–130 °C.

A VLE multistage model implemented in Visual Basic was used to evaluate the performance of the DECAB Plus process. The absorber and the stripper were modeled as a countercurrent cascade of equilibrium stages, and vapor–liquid partitions and compositions were calculated for each stage. Simulation results showed that the stripping temperature and RSF were the two main factors affecting the energy consumption for solvent regeneration. Higher reboiler temperatures led to lower specific reboiler duties, and the minimal heat duty was achieved at an RSF of 30%. Overall, the DECAB Plus process lowered the heat duty (2.4 GJ/t of CO₂) of the reboiler by 35% compared with the MEA process (3.7 GJ/t of CO₂). However, the DECAB Plus process required an additional approximately 0.96 GJ/t of CO₂ of heat to redissolve the precipitates, resulting in rather high energy consumption for the entire process. To make this process more competitive in energy efficiency, reducing or making use of the dissolution heat of the amino acid salt is critical.

5. Remarks and perspectives

The major challenges remain to identify a new generation of biphasic solvents and develop dedicated processes that can further reduce the energy penalty and lower the costs and equipment footprint. High CO₂ cyclic capacity, ideal phase equilibria behavior, fast absorption, low viscosity, high stability and low volatility all are regarded as critical

solvent properties to address these challenges.

5.1. Solvent screening based on property–performance relations and molecular modeling

Phase change solvents have attracted growing attention because they have great potential to reduce the energy penalty associated with CO₂ capture. Although multiple phase change solvents have been investigated, the selection of solvent components and formulations with respect to various performance criteria has generally been based on intensive experimental screening work. To lessen the intensity of solvent screening work, relationships between the solvent properties (such as base dissociation constants, *pK_a*, or hydrophobicity) and CO₂ capture performances (such as phase separation behavior, CO₂ loading capacity and desorption efficiency) should be explored [146].

In addition to experimental investigations, molecular modeling can serve a computational tool to help guide solvent performance screening for CO₂ capture as well as predict important physiochemical properties of solvents. Either quantum mechanical calculations (QM) such as density functional theory (DFT) *ab initio* approaches, molecular dynamics (MD) simulations, or Monte Carlo (MC) simulations may be used for this purpose. In general, QM methods can provide the information of electronic and structural properties, such as reaction energetics and free energies of reactants, products, and transition states, and structures of reaction species, which are necessary to understand reaction pathways and the effects of molecular structures. MD or MC simulations can be used to predict the dynamical behavior of molecules at reaction sites, the effects of solute–solvent interactions, and transport properties such as CO₂ diffusivity and solvent viscosity. Such information generated from molecular modeling can provide fundamental understandings of macroscopic scale phenomena such as CO₂ loading capacity, VLE, and *pK_a* at the molecular level, thus providing a link between solvent design and experimental data. A comprehensive review on applying various computational approaches to study CO₂ capture by aqueous amines has been published by Yang et al. [147]. Recently, a work on establishing molecular designs and quantitative structure–property relationships to develop water-lean solvents with low viscosity was reported [148].

Specific to phase change solvents, providing insight into tendency and efficiency of liquid–liquid phase separation represents a significant challenge for molecular modeling due to the time scale discrepancy between experiments and simulations. Phase separation is experimentally observed on the time scale of minutes, while classical approaches such as MD accesses hundreds of nanoseconds to microseconds at best (depending on the size of the system under consideration). This is because a small time step, on the order of femtoseconds, is required in simulations to integrate the equations of motion that advance a system to the final state. A range of techniques, applied to diverse sets of problems, were developed to circumvent this issue [149]. A steered molecular dynamics (SMD) technique may be useful for this purpose because it allows for systematic control of how one-phase reacted systems can be brought towards two-phase systems as a function of system's composition and concentration [149]. A key concept in SMD simulations is the implementation of an external constraint on selected atoms during the simulation and calculation of system's energy change as a result of that perturbation. During this transition, the constraint does work on the system (or vice versa), and the work calculated during the transition is a measure of the driving force behind the phase separation process. This concept may be explored to accelerate phase separation in studying phase change solvent systems to MD accessible time scales.

5.2. Analysis of ideal vapor–liquid equilibrium behavior

The VLE behavior is a critical solvent property because it determines the CO₂ cyclic capacity, the driving force for CO₂ absorption and the

attainable stripping pressure. However, complete VLE data are not always available for many of the biphasic solvents reported. Careful VLE measurement is necessary to reliably assess the energy performance of the absorption process. In general, an isothermal VLE curve can be approximated as a straight line on a semi-log plot with a logarithmic scale for CO_2 partial pressure. VLE curves can be catalogued, based on the gradient of the slope, into three types, as shown in Fig. 7a [150]. The smaller the slope, the higher the cyclic capacity that can be attained. Fig. 7b also illustrates the VLE curves of the rich- and lean-phase solvents after they are separated: the VLE curve of the rich phase, toward the right side of the dual-phase mixture solvent, has a more gradual slope, and that of the lean phase, toward the left side, has a steeper slope. This result indicates that the absorbed CO_2 is concentrated in the rich phase. When the CO_2 cyclic capacity, the potential viscosity of the rich phase and the effects of equipment corrosion and solvent degradation are considered, the second type of VLE (VLE2, with a moderate slope) shown in Fig. 7a is preferred for the CO_2 capture application.

In addition to the measurement of detailed VLE data, thermodynamic models, which are based on macroscopic, measurable properties as opposed to microscopic molecular models, can also be used to predict VLE data under various operating conditions. Typically, various thermodynamic models, such as the Kent–Eisenberg model, Deshmukh–Mather model, the specific ion interaction theory (SIT) model, the electrolyte–nonrandom two liquids (e-NRTL) model and the extended UNIQUAC model, have been used to predict VLE for homogeneous solvents [151–156]. The feasibility of using such models to predict VLE data for biphasic solvents needs to be validated and major modifications or new models are likely to be required to describe the dual-phase systems.

5.3. Parasitic power loss of phase change solvent-based processes

Most of the biphasic solvent screening and evaluation work has focused on the CO_2 absorption capacity and phase transitional behavior. However, the kinetics and thermodynamic performance of solvents have not been thoroughly investigated. The kinetics of absorption is well known to determine the footprint of the absorber, and VLE data significantly affect the energy penalty, both of which are critical in determining the costs of CO_2 capture. For several phase transitional absorption processes, the heat duty of the reboiler was estimated to be 35% lower than the benchmark MEA process. However, information on the total parasitic power loss, including the power use of blowers and pumps (W_{pmp}), the power loss caused by the reboiler heat duty (W_{reb}) and the CO_2 compression work requirement (W_{cmp}), has been not available in most of the researches reported. Among these factors, W_{reb} and W_{cmp} are the two major contributors, accounting for more than 80% of the total energy penalty. As discussed by Kim and Lee [150,157], the VLE data, absorption heat, temperature difference in the main cross-heat exchanger and partial pressure ratio of CO_2 (defined as the ratio of the equilibrium CO_2 partial pressure over the solvent to the CO_2 partial pressure of the flue gas, PR) in the absorber are the four dominant parameters affecting the total energy penalty. All these parameters affect the value of W_{reb} , whereas the VLE data, absorption heat and PR also relate to the stripping pressure and thus affect the value of W_{cmp} . The authors concluded that the energy penalty did not necessarily decrease with decreasing heat of absorption and that the optimal heat of absorption incurred the lowest energy penalty [150]. This is because a lower absorption heat will result in a lower CO_2 partial pressure in the CO_2 product stream exiting the stripper, as determined by the Gibbs–Helmholtz equation, and will thus increase W_{cmp} and affect W_{reb} (i.e., the net effect on W_{reb} depends on the combined effect of increasing stripping heat use and decreasing reaction heat demand). Therefore, an optimal heat of absorption exists, for which the sum of W_{cmp} and W_{reb} is minimal. Kim and Lee [150] revealed that the CO_2 loading in the rich phase was a critical factor influencing the energy demand for the generic biphasic solvent-based process. With increasing CO_2 loading in the rich phase, the energy penalty decreased. This finding was expected because a high stripping pressure can be achieved with a high CO_2 loading in the solvent feed, resulting in decreases in both W_{cmp} and the use of stripping heat (thus W_{reb}). Furthermore, for a given CO_2 loading in the rich-phase solvent, increasing the volumetric fraction of the rich-phase solvent will result in a decrease in energy penalty because of the high absorption capacity, thus reducing the sensible heat. Note that in practice, the volumetric fraction of the rich-phase solvent may increase with decreasing CO_2 loading in the rich phase because the unreacted amine is transferred from the lean phase to the rich phase. Therefore, a tradeoff between the CO_2 loading and the rich volume fraction should also be considered when selecting operating conditions. In addition, thermodynamic models for phase change systems are regarded as important for industrial equipment design. However, such thermodynamic models have seldom been studied for phase change systems. Ye and colleagues [158] recently reported a comprehensive thermodynamic model that could be used to predict phase equilibria and reaction heats of DETA–PMDETA biphasic solvent systems.

5.4. Reduction of viscosity of phase change solvents

The viscosity of amine-based solvents tends to increase dramatically with increasing CO_2 loading, especially when polyamines are used. The rich-phase solvent could become highly viscous because most of the absorbed CO_2 is concentrated in this phase. A high solvent viscosity would adversely affect the heat and mass transfer performance of the absorption process [159–161]. The liquid-side mass transfer coefficient (k_L) is inversely proportional to the viscosity (μ_L) to a power of approximately 0.9, based on a correction [Eq. (9)] developed by Hikita

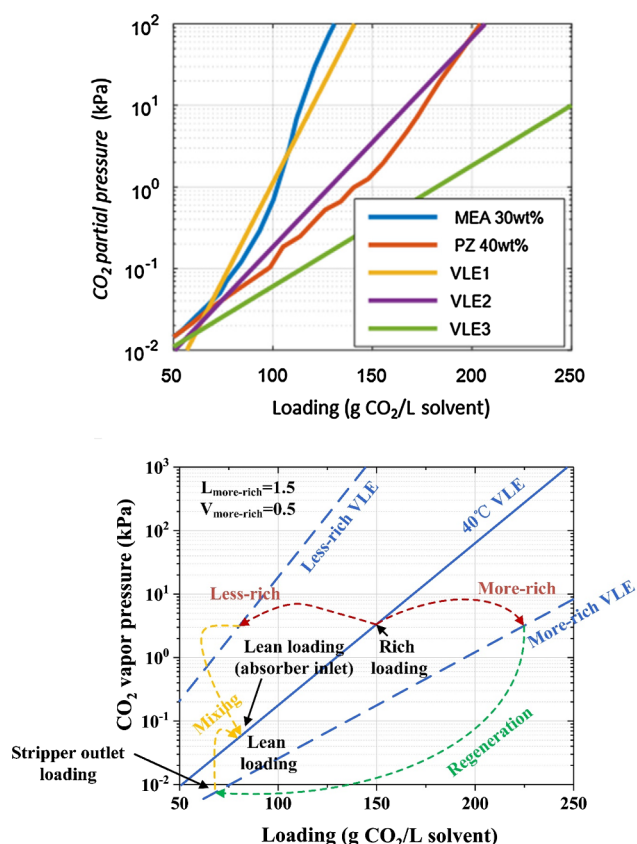


Fig. 7. (a) Assumed VLE curves for three hypothetical solvents; (b) VLE curves for a phase change solvent (solid line: solvent before separation of two liquid phases; dash lines: lean and rich phases after separation) [150]. Reproduced from ref. [150] with permission from Elsevier.

and Ishikawa [162] and the modified Einstein correlation [Eq. (10)].

$$k_L \propto \left(\frac{1}{\mu_L} \right)^{0.37} (D_L)^{0.67} \quad (9)$$

$$D_L \propto \left(\frac{1}{\mu_L} \right)^{0.8} \quad (10)$$

Similarly, according to the correlation recommended by Dittus and Boelter [163], the heat transfer coefficient (h) is inversely proportional to the viscosity to the power of 0.4. However, few literature studies report viscosity data for biphasic solvents. Our measurements showed that the viscosity of the rich-phase solvents could reach as high as several hundred centipoise, which is 2 orders of magnitude higher than that of the benchmark MEA solvent. Accordingly, the mass transfer and heat transfer coefficients could be one order of magnitude lower than those for the MEA solvent, requiring a larger-sized absorber and heat exchanger. Attention should thus be paid to mitigating the excess solvent viscosity to maintain rapid mass and heat transfer rates and minimize the equipment footprint and costs.

It should be noted that viscosity significantly increases with CO₂ loading because of the hydrogen-bonding between neighboring zwitterions. As reported by Glezakou et al. [62,164,165], molecular structures, that promote internal hydrogen bonding (within the same molecule) and suppress interactions with neighboring molecules, have low viscosities. In addition, for the internal hydrogen bonding, tuning the acid properties of amine leads to a shift of the acid/zwitterion equilibrium toward a non-charged acid state can further reduce the viscosity. Although the above strategies for the reduction of the CO₂-rich solution was obtained from the water-lean carbon capture solvent system, it can also give some insight for the development of the biphasic solvent with a low viscosity.

5.5. Stability, volatility and toxicity of phase change solvents

The stability and volatility of biphasic solvents are also critical for practical applications. However, few robust tests have been conducted to assess the thermal stability and oxidative degradation of the reported biphasic solvents. The biphasic solvents that showed other favorable properties, as reported above, may not be stable under the chosen absorption and stripping conditions. Typically, the rates of both thermal and oxidative degradation increase with CO₂ loading and operating temperature [166–174]. Furthermore, an amine blend solvent tends to be less stable than its single component counterparts because the degradation product from one solvent component may react with that from another component [175,176]. As Rochelle reported [177], primary and secondary amines degrade at a comparably low temperature (100–130 °C) because of the formation of cyclic oxazolidinones and ureas from their carbamates. Tertiary amines with the absence of methyl and ethanol groups are more stable at elevated temperatures. Because cyclic and long-chain diamines are less likely to produce cyclic urea at the typical stripping temperatures, they may possess good thermal stability. Steric hindrance groups in amines retard the attack on their adjunct amino groups, resulting in a more thermally stable structure. Furthermore, ether amines exhibit better thermal stability than their alkanolamine counterparts because carbamate polymerization may not occur. The oxidative stability is affected by the oxygen partial pressure, CO₂ loading, amine concentration and temperature. Generally, tertiary amines are more stable than secondary amines and then primary amines in oxygen-containing environments [178–180].

Solvent volatility depends on the types of functional groups contained in the amine structures [174,181,182]. The presence of polar functional groups, such as –NH₂ and –OH, lowers the volatility, whereas the presence of nonpolar functional groups, such as –CH₃ and –CH₂, increases the volatility. In addition, the competition between intramolecular and intermolecular hydrogen bonds plays an important

role in the volatility of amines. The formation of an intermolecular hydrogen bond between an amine and water is preferred for low volatility [183]. Among the polar functional groups, a cyclic–OH performs the best in terms of reducing volatility [174]. Compared with primary and secondary amines, the volatility of tertiary and hindered amines should be carefully examined because a portion of these amines cannot be converted to nonvolatile ions through reactions with CO₂. Du et al. [174] developed a mathematical model based on a functional group contribution approach to predict the Henry's law constants for CO₂ dissolution in aqueous solutions, which can be used to estimate the volatility of aqueous amine solutions. The development and evaluation of new biphasic solvents should factor in solvent stability and volatility as important criteria.

Wastes from solvent degradation, volatile emissions, and accidental spills tend to be toxic and can cause potential concerns to human health and the environment. Increasing attention has been drawn to the health and environmental impact of amine-based scrubbing solvents in recent years. The formation of nitrosamines and nitramines, in both liquid and vapor phases, from amine solvents is of particular importance for such concerns [184]. Veltman and co-workers reported that CO₂ scrubbing could result in a 10-fold increase in toxic impact on freshwater ecosystems due to MEA vapor emissions [185]. Thitakamol et al. [186] identified potential contaminants from conventional chemical and physical CO₂ scrubbing solvents and provided potential implications to human health and the environment by examining the toxicological information obtained from the Material Safety Data Sheets for all substances involved. Schreiber et al. [187] suggested that life cycle approaches would be necessary to get a holistic evaluation on environmental toxicity. To the best of our knowledge, all reported research has addressed conventional monophasic solvents – no such reports are available for phase change solvents. In general, amines or amine-like materials as well as solubilizing components reported in formulating biphasic solvents have been of the same types as those used in conventional monophasic solvents. Therefore, phase change solvents are not expected to be significantly different from monophasic solvents with respect to toxicity. However, given that phase change solvents are emerging materials and new formulas are applied, gaining an understanding of their toxicity is of great importance for solvent development for practical purposes.

5.6. Development of nonaqueous phase change solvents

Compared with aqueous solvents, nonaqueous solvents have the advantages of low heat capacity, low absorption heat and no stripping heat use, which are beneficial to further reduce the parasitic energy loss [188–190]. The use of organic solvents may also lessen equipment corrosion and reduce amine degradation and evaporation losses because a comparably low stripping temperature is required. Although a few nonaqueous biphasic solvents have been reported in the literature, the related processes for CO₂ capture have not been fully assessed. For practical application, one major issue related to the nonaqueous biphasic solvent-based process is water management because of the presence of water vapor (~10 vol%) in the flue gas. Thus, the concerns of how water can be balanced in the process, how water condensate affects the solvent performance and how water can be separated and removed from the solvent must be addressed. Note that water may accumulate in the solvent, which may offset the potential advantage of using a nonaqueous biphasic solvent. This problem can be solved by deploying a dehumidification system before the flue gas enters the absorber, but this step may be energy intensive and costly. Lait et al. [191] developed a nonaqueous biphasic solvent from a hydrophobic amidine or guanidine paired with an alcohol or amine. In their process, the nonaqueous CO₂-rich phase was separated from water, thus preventing water from accumulating in the solvent used for CO₂ stripping [191]. As a result, water balancing and management were able to be achieved without flue gas dehumidification [191].

5.7. Liquid–liquid phase separation equipment

A phase separator is dedicated equipment within the biphasic solvent-enabled process. The residence time required for the CO₂-rich phase to settle and separate from the spent solvent determines the size of the phase separator. The efficiency of phase separation determines the purity of the separated liquids and affects the downstream stripper. Although little work has been reported on the liquid–liquid phase separation equipment for the CO₂ capture application, this equipment has been intensively investigated in the chemical industry for the separation of liquid–liquid mixtures [192–196]. Gravity and annular centrifugal separators are two typical setups for these types of equipment [197–200]. The cost of a gravity separator is comparably low, whereas an annular centrifugal separator is preferred for systems requiring a low residence time. Coalescence and the settling of liquid drops are two critical processes for separation. Generally, the separation efficiency is dependent on the density difference between the two liquid phases, the viscosity of the separated solvents, the size of the settling drops and the coalescing behavior of the two phases [196]. As Leonard et al. reported [201], the dispersion number, defined as the ratio of the settling time of liquid drops to the solvent residence time in the separator, is a critical parameter for evaluating the separation performance of the solvent. Dispersion numbers of 0.0001, 0.0004, 0.0008 and 0.0016 (dimensionless) represent poor, fair, good and excellent separation, respectively [201]. Several empirical correlations that take into account the selected solvent properties and geometrical parameters are available to predict the dispersion number [196]. These correlations can provide relevant insights into the design of phase separators dedicated to the biphasic solvent-enabled process.

5.8. Integration of phase change CO₂ absorption process with power plants

Many current R&D activities are focused on developing and improving biphasic solvents and processes. When applied to a power plant, the performance and acceptance of a CO₂ capture technology will also depend on how it is integrated into the power plant and how it affects the plant operability. Similar to other capture technologies, a few interfaces with a power plant have to be considered and optimized:

- Conditions of steam extraction from the power plant steam cycle;
- Cooling requirements of carbon capture process and the related heat recovery and integration with the power plant;
- Heat recovery associated with CO₂ compression;
- CO₂ capture-ready flue gas and power plant flue gas desulfurization (FGD) and other gas cleaning devices;
- Wastewater treatment and waste disposal.

The reduction in power plant efficiency by CO₂ capture can be minimized by optimizing the integration of relevant heat uses (e.g., steam extraction for solvent regeneration) and heat sources (e.g., heat recovery from the compressor and capture units). The heat use for solvent regeneration, mostly by steam extracted at the crossover of the intermediate- and low-pressure turbines from the power plant, is critical in this regard. However, the conventional carbon capture system and the standard power plant steam cycle are optimized independently, indicating that the plant combined with carbon capture tends not to be optimal for energy efficient. Thus, a better option to integrate the carbon capture system into the power plant, including both the heat uses and heat sources as specific to the properties of biphasic solvents and the related processes, must be identified.

In addition, interfacing with the power plant FGD unit needs special attention. It is likely that the flue gas SO₂ concentration from the FGD (e.g., 50–200 ppmv depending on the coal used) is required to be reduced to a low level (e.g., < 10 ppmv) by installing a separate polishing scrubber or upgrading the existing FGD unit. Ideally, biphasic solvents that tolerate high levels of SO₂ in the flue gas, or can be easily

reclaimed when degraded with SO₂ are favorable for the capture application, resulting in no or few retrofitting requirements to FGD.

5.9. Assessment of technical and economic feasibility

Technical and economic feasibility of conventional monophasic solvent-based absorption technologies for the PCC application has been widely assessed. In a recent study, Mantripragada et al. estimated that the cost of CO₂ capture varied from \$43–73/tonne depending on steam supply configurations for capturing 90% of the CO₂ emissions from a 650 MWe (primary gross) power plant [202]. As described afore, dozens of monophasic absorption technologies have been tested at laboratory-, bench-, small pilot-, and large pilot-scales. At present, there are two absorption processes in commercial deployment for PCC, including one to treat the flue gas from a 160 MWe full-scale unit at Boundary Dam power plant in Canada and the other to treat a 240 MW slipstream of flue gas from Petra Nova power plant in the U.S., both of which use amine-based solvents to remove 90% of the CO₂ from coal combustion flue gas [203].

In comparison with conventional monophasic absorption technologies, most of the reported biphasic solvent-based technologies were laboratory developments. Only a limited number of the biphasic solvent-based technologies, such as the iCap and DMX process as discussed in Section 4, were demonstrated in actual industrial environments, and even such efforts have been limited to bench- or small pilot-scales. This is because the biphasic solvent research is a relatively new area as evidenced by the first known patent published just a dozen of years ago [204]. Therefore, the techno-economic feasibility of biphasic solvent-based absorption processes have not been well demonstrated, and more scale-up demonstration studies are required to prove their technical, economic, as well as environmental advantages and to establish a techno-economic basis for technology assessment.

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Conflict of interest

The authors declare that they have no competing financial interests.

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